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Monsanto Research Corp, Dayton, OH

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The report describes a study of air emissions, water effluents, and solid residues resulting from the manufacture of phosphate fertilizers. It includes the production of wet process phosphoric acid, superphosphoric acid, normal superphosphate, triple superphosphate, and ammonium phosphate. Air emissions from production of phosphate fertilizers include particulates, fluorides, ammonia, and sulfur oxides. Phosphate fertilizer plants control air emissions by a combination of cyclones, baghouses, and wet scrubbers. Material handling operations are generally enclosed to reduce fugitive particulate emissions. Only fluoride emissions from curing and storage at normal superphosphate plants are typically uncontrolled. Water effluents from the production operations arise from wet scrubbers, barometric condensers, steam ejectors, gypsum slurry, and acid sludge. Noncontact cooling water is normally segregated from other wastewater streams. Wastewaters are contaminated with phosphates, fluorides, sulfates and gypsum. Process water is discharged to large gypsum ponds for storage and recycle; it is normally not discharged to surface streams. Solid residues generated at phosphoric acid plants are gypsum from the filtration of wet process phosphoric acid, wet process phosphoric acid sludge, and solids suspended in the wet scrubber liquor.

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Research Triangle Park, NC 27711

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PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for development of needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility to develop control technology for a large number of operations (more than 500) in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgement, sufficient environmental risk associated with the process to invest in the development of control technology. This report on the phosphate fertilizer industry contains data necessary to make that decision for the air, water, and solid waste discharges resulting from the production of phosphoric acid and superphosphoric acid, normal and triple superphosphate fertilizer, and granular ammonium phosphate fertilizer.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's reponsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of the phosphate fertilizer industry. Dr. R. A. Venezia served as EPA Task Officer.

ABSTRACT

This report describes a study of air emissions, water effluents, and solid residues resulting from the manufacture of phosphate fertilizers. It includes the production of wet process phosphoric acid, superphosphoric acid, normal superphosphate, triple superphosphate, and ammonium phosphate. The potential environmental impact of the industry is evaluated on a multimedia basis.

Air emissions from production of phosphate fertilizers include particulates, fluorides, ammonia, and sulfur oxides. The potential environmental effect of these emissions is evaluated by calculating the source severity, defined as the ratio of the time-averaged maximum ground level concentration of a pollutant to a hazard factor. For particulate and sulfur oxide emissions, the hazard factor is the primary ambient air quality standard; for fluoride and ammonia emissions, it is a reduced threshold limit value. Source severity values for emissions from the wet scrubber system at an average phosphoric acid process are 0.18 for fluorides and below 0.05 for particulates and sulfur oxides. For superphosphoric acid, severity is 0.09 for fluoride and below 0.05 for particulates. For ammonium phosphate, severities are 0.43 for particulate, 0.45 for fluoride, and 0.09 for ammonia. For normal superphosphate, source severity ranges from 0.004 to 0.35 for particulate and from 0.18 to 7.2 for fluoride. For run-of-the-pile triple superphosphate, particulate source severity ranges from 0.009 to 0.04, and fluoride source severity is 0.77. For granular triple superphosphate, particulate source severity ranges from 0.004 to 0.06, fluoride source severity ranges from 0.12 to 0.36, and SO_x source severity is 0.11.

Phosphate fertilizer plants control air emissions by a combinaation of cyclones, baghouses, and wet scrubbers. Material handling operations are generally enclosed to reduce fugitive particulate emissions. Only fluoride emissions from curing and storage at normal superphosphate plants are typically uncontrolled.

Water effluents from the production operation arise from wet scrubbers, barometric condensers, steam jet ejectors, gypsum slurry, and acid sludge. Noncontact cooling water is normally segregated from other wastewater streams. Wastewaters are contaminated with phosphates, fluorides, sulfates, and gypsum. Process water is discharged to large gypsum ponds for storage and recycle; it is normally not discharged to surface streams.

Solid residues generated at phosphoric acid plants are gypsum from the filtration of wet process phosphoric acid, wet process phosphoric acid sludge, and solids suspended in the wet scrubber liquor. These solid waste residues are, for the most part, stored in ponds, stacked in piles, or stored in mining pits on site.

This report was submitted in partial fulfillment of Contract 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study covers the period May 1976 to March 1979.

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ABBREVIATIONS AND SYMBOLS

AAQS -- ambient air quality standard

APP -- ammonium polyphosphate

BPL -- bone phosphate of lime or tricalcium phosphate

C_D -- concentration of particular pollutant, g/m^3

D -- distance downwind from source, m

DAP -- diammonium phosphate

e - 2.72

$E_{D/C}$ -- emission factor for dryer/cooler

E_P -- emission factor for product sizing and material transfer

$E_{R/A}$ -- emission factor for reactor/ammoniator-granulator

E_{TOTAL} -- composite emission factor

E_{TP} -- emission factor for total plant

F -- hazard factor

GNSP -- granular normal superphosphate

GTSP -- granular triple superphosphate

h - emission height, m

MAP -- monoammonium phosphate

$N_{D/C}$ -- number of emission factors for dryer/cooler

NEDS -- National Emissions Data System

NO_x -- nitrogen oxides

N_P -- number of emission factors for product sizing and material transfer

N-P-K -- nitrogen-phosphorus-potassium fertilizer

$N_{R/A}$ -- number of emission factors for reactor/ammoniator-granulator

NSP -- normal superphosphate

N_{TP} -- number of emission factors for total plant

P_2O_5 -- phosphorus pentoxide, used to express the phosphorus content of fertilizer

ABBREVIATIONS AND SYMBOLS (continued)

ppb -- parts per billion
Q -- mass emission rate, g/s
R -- amount of rock required to produce 1 metric ton of NSP
ROP -- run of pile
ROP-NSP -- run-of-pile normal superphosphate
ROP-TSP -- run-of-pile triple superphosphate
S -- source severity
SO_x -- sulfur oxides
SPA -- superphosphoric acid
t -- averaging time, min
t_o -- instantaneous averaging time, 3 min
TLV -- threshold limit value
TSP -- triple superphosphate
TVA -- Tennessee Valley Authority
$\bar{u}$ -- national average wind speed, 4.5 m/s
V_D -- wastewater effluent flow rate, m^3/s
V_R -- volumetric flow rate of receiving body above plant discharge, m^3/s
x -- downwind dispersion distance from a source of emissions
WPPA -- wet process phosphoric acid
$x_{0.1}$ -- downwind distance from an emission source at which $\bar{\chi}/F=0.1$
$x_{1.0}$ -- downwind distance from an emission source at which $\bar{\chi}/F=1.0$
π -- 3.14
σ_y -- $0.2089\ x^{0.9031}$
σ_z -- $0.113\ x^{0.911}$
χ -- downwind ground level concentration at reference coordinate with emission height of h
$\bar{\chi}$ -- time-averaged ground level concentration
χ_{max} -- instantaneous maximum ground level concentration
$\bar{\chi}_{max}$ -- time-averaged maximum ground level concentration

SECTION I

INTRODUCTION

The phosphate fertilizer industry converts insoluble phosphate rock into water soluble fertilizers that are rich in phosphorus and readily available for plant uptake. For this program, the phosphate fertilizer industry is considered to include the production of phosphoric acid by the wet process (reaction of phosphate rock with sulfuric acid), the concentration of phosphoric acid to superphosphoric acid, the production of normal and triple superphosphates, and the manufacture of granular ammonium phosphates. Phosphoric and superphosphoric acids serve as intermediates in the production of final fertilizer materials.

Historically, phosphate fertilizers have been one of the large volume chemicals produced in the United States. Production is concentrated in the state of Florida because of its extensive phosphate rock deposits. Until the early 1960's, superphosphates were the primary phosphate fertilizer material manufactured, but now ammonium phosphates predominate because of their higher overall nutrient content.

During phosphate fertilizer production, air emissions, water effluents, and solid residues are released into the environment. This assessment document characterizes these discharges and evaluates their potential environmental impact. The report contains a source description that defines process operations, process chemistry, plant production and capacity, and industry locations. Emission points are identified, emission species are characterized, and average emission rates are determined, all on a multimedia basis. Present and emerging control technologies are also considered in terms of their effectiveness, advantages/disadvantages, and extent of application. The final section of the report discusses the growth and nature of the phosphate fertilizer industry.

SECTION 2

SUMMARY

In 1975 the phosphate fertilizer industry in the United States consumed 26.1 x 10^6 metric tons of phosphate rock to produce approximately 4.89 x 10^6 metric tons of phosphate fertilizer. Final products included 0.44 x 10^6 metric tons of run-of-the-pile normal superphosphate, 0.90 x 10^6 metric tons of granular triple superphosphate, 0.60 x 10^6 metric tons of ammonium phosphates, all expressed in terms of their phosphorus pentoxide (P_2O_5) content. In addition, 6.29 x 10^6 metric tons of wet process phosphoric acid and 0.506 x 10^6 metric tons of superphosphoric acid were manufactured as phosphate fertilizer intermediates.

Phosphate fertilizers are produced at 121 plants located in 28 states. The number of plants producing each compound and the average production rates are given in Table 1. Approximately 30% of the plants are complexes producing more than one phosphate material. These same plants account for the majority of production volume. Florida, because of its large phosphate rock deposits, is the leader in number of plants (i.e., 16) and tonnage of materials manufactured.

TABLE 1. PRODUCTION STATISTICS FOR PHOSPHATE FERTILIZER PLANTS

Product	Number of plants	Average plant production rate, metric tons/yr (P_2O_5 basis)
Wet process phosphoric acid	36	175,000
Superphosphoric acid	9	56,200
Ammonium phosphate	48	75,000
Normal superphosphate	66	6,650
Granular triple superphosphate	13	69,100
Run-of-the-pile triple superphosphate	10	59,700
Total industry	121[a]	NA[b]

[a] Some plants produce more than one product.

[b] Not applicable.

Phosphate fertilizer production begins with phosphate rock containing 30% to 35% P_2O_5. This rock is crushed and mixed with aqueous sulfuric acid to produce phosphoric acid (28% to 32% P_2O_5). The reaction takes place in an attack vessel; in addition to phosphoric acid, insoluble calcium sulfate dihydrate (gypsum) and fluorine compounds are produced. Precipitated gypsum is filtered from the acid, sluiced with recycled pond water, and pumped to a gypsum pond. Fumes from the attack vessel are vented to a packed-bed wet scrubber for fluoride removal before they are vented to the atmosphere. The low quality (28% to 32% P_2O_5) acid is concentrated to 54% P_2O_5 by evaporation.

Superphosphoric acid (P_2O_5 greater than or equal to 66%) is produced by further concentrating the 54% wet process phosphoric acid using either vacuum evaporation with heat transfer surfaces or submerged combustion/direct heating. All processing steps are vented to a common scrubber system to remove fluorides and particulates. Gypsum pond water is used as the scrubbing liquid and then returned to the pond.

The term normal superphosphate is used to designate a fertilizer material containing from 16% to 21% P_2O_5 made by reacting ground phosphate rock and sulfuric acid. Rock and acid are mixed in a reaction vessel, held in an enclosed area (den) during the solidification process, and transferred to a storage pile for curing. Cyclones and baghouses are used to control particulate emissions from rock processing operations; scrubbers are used to reduce fluoride and particulate emissions from the reactor and den. However, no controls are normally employed on the curing building because of the lower level of emissions and typically small plant size.

Triple superphosphate designates a fertilizer material having a P_2O_5 content of over 40% made by reacting phosphate rock and phosphoric acid. There are two principal types of triple superphosphate: run-of-the-pile and granular. Run-of-the-pile material is essentially a nonuniform pulverized mass produced in a manner similar to that used for normal superphosphate production. In the production of granular triple superphosphate, a liquid mixture of rock and acid is distributed onto a bed of recycled fines in a granulator to produce a hard, uniform, pelletized granule. Cyclones, baghouses, and scrubbers are used to control particulate and fluoride emissions from the various processing steps.

In the manufacture of ammonium phosphates, phosphoric acid and ammonia are initially reacted in a preneutralizer to an ammonia/phosphoric acid mole ratio of approximately 1.4. The resulting slurry passes to an ammoniator-granulator, where the injection of additional ammonia causes further solidification. Ammonium phosphate granules are then dried, cooled, screened, and sent to product shipment. Exhaust streams from the preneutralizer and ammoniator-granulator pass through a primary scrubber in which phosphoric acid removes ammonia and particulate. Exhaust gases from the dryer, cooler, and screen go to cyclones for particulate removal. Materials collected in the primary scrubber and cyclones are returned to the process. The exhaust is sent to secondary scrubbers where recycled gypsum pond water is used as a scrubbing liquid to control fluoride emissions. The scrubber effluent is returned to the gypsum pond.

A summary of air emissions for the six production processes is presented in Table 2. For each emission point, the emission species and emission factors are reported. In addition to the process emissions at phosphate fertilizer plants, fluorine in the gypsum pond water is volatilized and emitted to the atmosphere as some form of fluoride.

In order to help evaluate the potential environmental impacts of air emissions and water effluents, certain criteria were used: source severity, affected population, and state and national emission burdens. The intent was to compare the relative impacts of a large number of source types studied. In evaluating potential environmental effects, average parameters have primarily been employed (e.g., emission factors, stack heights, population densities). A more detailed plant-by-plant evaluation was beyond the scope of the project and conclusions are not drawn with regard to actual environmental impacts at specific sites. In some cases, hazard factors used in the evaluation may be conservative due to a lack of more definitive health effects data.

Source severity (S) for air emissions compares the time-averaged maximum ground level concentration of an emitted pollutant, $\overline{\chi}_{max}$, to an estimated hazard factor, F, and is defined as $\overline{\chi}_{max}/F$. Values of $\overline{\chi}_{max}$ were calculated from average plants from accepted plume dispersion equations and the emission factors in Table 2. The hazard factor, F, is defined as the primary ambient air quality standard (AAQS) for criteria pollutants (particulates and sulfur dioxide). For fluoride and ammonia emissions, F is defined in terms of the reduced threshold limit value (TLV®): F = TLV(8/24)(1/100), where the factor 8/24 corrects for 24-hr exposure and 1/100 is a safety factor. Calculated source severity values are shown in Table 2.

Values for $\overline{\chi}_{max}$ could not be determined for hydrogen fluoride emissions from gypsum ponds. Instead, plume dispersion equations were used to determine the distances downwind from the pond at which the time-averaged pollutant concentration, $\overline{\chi}$, divided by F was below 1.0 and 0.05.

The potential environmental impact was also measured by determining the population around a plant exposed to a contaminant concentration exceeding an acceptable level. The affected population is defined as the number of persons living in the area around an average plant where $\overline{\chi}$ divided by F is greater than 1.0. Plume dispersion equations are used to find this

TABLE 2. EMISSION CHARACTERISTICS FOR PHOSPHATE FERTILIZER PROCESSES AT AVERAGE PLANTS

Process	Emission point	Emission species	Controlled emission factor, g/kg P_2O_5	Source severity[a]	Affected population, persons	
					S > 1.0	S > 0.05
Phosphoric acid	Rock unloading	Particulate	0.15 ± 250%	0.41	0	64
	Rock transfer and storage	Particulate	0.045 ± 180%	0.040	0	2
	Wet scrubber system	Particulate	0.054 ± 164%	0.025	0	0
		Fluoride	0.010 ± 47%	0.18	0	159
		Sulfur oxides	0.032 ± 200%	0.011	0	0
Superphosphoric acid	Wet scrubber	Particulate	0.011 to 0.055	0.01	0	0
		Fluoride	0.0073[b]	0.09	0	28
Ammonium phosphate	Total process[c] emissions	Particulate	1.5 ± 69%	0.43	0	288
		Fluoride	0.038 ± 30%	0.44	0	285
		Ammonia	0.068 ± 75%	0.09	0	41
Normal superphosphate	Rock unloading	Particulate	0.28[b]	0.02	0	0
	Rock feeding	Particulate	0.055 ± 180%	0.004	0	0
	Mixer and den	Particulate	0.26 ± 86%	0.013	0	0
		Fluoride	0.10 ± 120%	0.18	0	529
	Curing building[d]	Particulate	3.6[b]	0.35	0	519
		Fluoride	1.9 ± 120%	7.2	539	13,021
Run-of-the-pile triple superphosphate	Rock unloading	Particulate	0.07[b]	0.04	0	5
	Rock feeding	Particulate	0.014 ± 170%	0.009	0	0
	Cone mixer, den, and curing building	Particulate	0.16 ± 50%	0.03	0	0
		Fluoride	0.10 ± 40%	0.77	0	1,178
Granular triple superphosphate	Rock unloading	Particulate	0.09[b]	0.06	0	15
	Rock feeding	Particulate	0.017 ± 180%	0.01	0	0
	Reactor, granulator dryer, cooler, and screens	Particulate	0.05 ± 320%	0.004	0	0
		Fluoride	0.12 ± 30%	0.36	0	1,356
		Sulfur oxides	1.86[e]	0.11	0	307
	Curing building	Particulate	0.10 ± 240%	0.02	0	0
		Fluoride	0.018 ± 40%	0.12	0	161
Fertilizer complex	Gypsum pond	Fluoride	0.50 (0.025 to 2.5)[f]	1.0 @D = 1300 m 0.05 @D = 6700 m	0	5,532

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[a] Severity for fluoride based on TLV for hydrogen fluoride of 2.0 mg/m^3; severity for ammonia based on its TLV of 18 mg/m^3.

[b] Only two data points.

[c] Average process controlled by integrated control system with a single emission point.

[d] Uncontrolled emission factors because curing building emissions are not normally controlled.

[e] Worst case estimate based on fuel oil sulfur content.

[f] Emissions from gypsum pond are uncontrolled and vary widely depending on pond conditions.

area, which is then multiplied by an average population density to determine the affected population. Due to uncertainties inherent in sampling and dispersion modeling methodologies, the number of persons exposed to a $\overline{\chi}/F$ ratio greater than 0.05 is also reported. Values for the affected population are reported in Table 2.

Another measure of potential environmental impact is the total mass of industry emissions of each criteria pollutant. These values were compared to total state and national emissions from all sources to find the emissions burden due to various segments of the phosphate fertilizer industry. The percent contributions to states' emissions burdens by wet process phosphoric acid plants ranged from 0.004% to 0.4% for particulates and from 0.0002% to 0.02% for sulfur dioxide. On a national basis, wet process phosphoric acid plants contributed 0.01% of the nation's particulate burden and less than 0.001% of the sulfur dioxide burden. Particulate emissions from superphosphoric acid plants contributed from less than 0.001% to 0.005% of each state's emissions burden. For normal and triple superphosphate production, it was found that in each state and on a national basis the particulate and sulfur oxide (SO_x) contribution to the respective emissions burden was less than 0.001%. Ammonium phosphate particulate emissions represent approximately 0.02% of the total national particulate emissions burden from all sources. On a statewide basis, ammonium phosphate production contributed 0.1% or more of the total statewide particulate emissions burden in only Florida (0.8%), Idaho (0.4%), and Louisiana (0.3%).

Environmental and economic concerns have prompted use of control devices in most facets of the wet process phosphoric and superphosphoric acid industry, with the exception of volatile emissions from the gypsum pond. Rock unloading, rock transfer, and rock charging operations are located in partially enclosed structures with ventilation systems venting to baghouses for rock recovery. Vaporous and particulate emissions issuing from the attack vessel, filtration system, and clarifier are all vented to a common venturi throad packed-bed wet scrubber. Recycled pond water is used in the scrubber to remove emission species and is then sent back to the gypsum pond. A similar wet scrubbing system is used as superphosphoric acid plants to remove fluoride and particulate emission species.

The types of air pollution control equipment used at superphosphate plants are varied; however, all plants have a basic emissions control system consisting of cyclones, baghouses, and wet scrubbers. All plants use cyclones and/or baghouses to control particulate emissions from the rock unloading and rock feeder systems. Wet scrubbers are used to control particulate and fluoride emissions from the mixer den, curing building, reactor, granulator, dryer, and cooler. These scrubbers also control SO_x emissions from the dryer at granular triple superphosphate plants when fuel oil is used. Only the fluoride emissions from the curing and storage building at normal superphosphate plants are uncontrolled.

Stack emission from all ammonium phosphate plants have some type of emission control. Cyclones are used for product recovery, and wet scrubbers are used for ammonia (NH_3), fluoride, and product recovery.

Based on industry production trends and forecasts, production of wet process phosphoric acid and superphosphoric acid are expected to increase at annual rates of 4% to 7% and 7% to 10%, respectively. Normal superphosphate production is expected to decline by 1% to 5% until about 1982 when industry production is expected to stabilize. Triple superphosphates, both granular and run-of-the-pile, are expected to maintain a moderate annual growth rate of 2%. Ammonium phosphate production from 1975 to 1980 is projected to grow at an annual rate of 7.5%, resulting in approximately 44% more production in 1980 than in 1975. If the current level of emission control is maintained, emissions from these production processes will increase or decrease in a similar fashion.

Sources of process wastewater from wet process phosphoric acid production include wet scrubber liquor, gypsum slurry water, and barometric condensers. Gypsum pond water normally supplies most of the water requirements for operation of wet scrubbers and barometric condensers and also for transferring the waste gypsum to a disposal area although variations do exist. Acid sludge, generated in acid clarification, contains substantial amounts of phosphate and is normally disposed of by blending into dry fertilizer. Cooling water may be recirculated gypsum pond water. If supplied by a segregated nonprocess system instead, it may be recycled or discharged. Steam condensate which is contaminated, such as that from barometric condensers and vacuum ejectors, is discharged to the gypsum pond. Uncontaminated steam condensate is discharged to receiving waters without treatment. Wastewater streams contain varying quantities of phosphoric acid (H_3PO_4), fluorides, sulfates, and gypsum.

Wastewater streams at superphosphoric acid plants come from barometric condensers, steam jet ejectors, and wet scrubbers. These streams contain quantities of H_3PO_4 and fluorides. Wastewater from superphosphoric acid plants is normally contained in a manner similar to that used at wet process phosphoric acid plants.

The only source of wastewater at normal and triple superphosphate fertilizer plants is the scrubber liquors. Scrubber systems use recycled water from the gypsum ponds or other holding reservoirs. Nearly all triple superphosphate plants are located at fertilizer complexes producing wet process phosphoric acid and, as a result, use gypsum pond water in their scrubber systems. More than 60% of normal superphosphate plants now practice fluorine recovery and thereby eliminate or greatly reduce the need for a pond.

Plants recovering fluosilicic acid consume the small amount of silica-containing liquid waste generated as a filler in fertilizer production.

Ammonium phosphate production facilities occasionally use secondary wet scrubbers to remove fluorides and other contaminants from process gas streams after preliminary scrubbing with a weak phosphoric acid solution for ammonia recovery. Secondary scrubbers use recycled water from gypsum ponds or other holding reservoirs.

In a study of over 70% of the plants in the phosphate fertilizer industry, nearly 75% reported no discharge of process wastewater. Of the 15 plants that reported a discharge, 12 reported a discharge only when necessitated by excessive rainfall. Several of these reported that they have not treated or discharged water for several years. In actual practice, discharge of contaminated process water from the recycle pond system is held to an absolute minimum due to treatment costs.

One plant was found to use river water on a once through basis for scrubbing air emissions and for cooling. Effluent from this plant is discharged without treatment.

Available wastewater discharge data from seven plants on file as of October 1976 at the Florida Department of Environmental Regulation were collected and analyzed by means of a water source severity relationship.

Source severity for water effluents compares the concentration of a particular pollutant after discharge and dilution in the receiving body with an estimated allowable concentration denoted as the hazard factor.

In determining the source severity of a plant, the discharge quantity is compared to the receiving body flow rate times the hazard factor according to the following equation:

$$S = \frac{V_D\ C_D}{\left(V_F + V_D\right)F} \qquad (1)$$

where S = source severity for a particular pollutant

V_D = wastewater effluent flow rate, m^3/s

C_D = concentration of particular pollutant, g/m^3

V_R = volumetric flow rate of receiving body above plant discharge, m^3/s

F = hazard factor for particular pollutant, g/m^3

Severities for fluoride, phosphorus, and to a lesser degree ammonia-nitrogen in discharged waters were found in a number of cases to be above 1.0. This was due to the extremely low flow rates of the receiving bodies and should represent a worst case analysis for the small number of plants that do discharge.

Solid residues generated at phosphoric acid plants are gypsum from the filtration of wet process phosphoric acid, wet process phosphoric acid sludge, and solids suspended in the wet scrubber liquor. These solid waste residues are, for the most part stored in ponds, stacked in piles, or stored in mining pits on site. A small percentage (approximately equal to 1%) is used as a raw material for various products. Under normal conditions, the solid residues cause no adverse environmental effects. At normal and triple superphosphate plants, solid residues are in the form of slurries from the wet scrubber and are therefore included with wastewater treatment practices.

SECTION 3

SOURCE DESCRIPTION

A. OVERVIEW OF PHOSPHATE FERTILIZER INDUSTRY

Phosphorus is one of the major elements essential for normal plant growth (1). Naturally occurring phosphorus in phosphate rock in the form of tricalcium phosphate is almost completely insoluble in water (solubility in cold water equals 20 g/m^3 of water) (2). To enhance plant growth, the phosphate fertilizer industry converts insoluble phosphate rock into water-soluble fertilizer products.

1. Phosphate Rock Consumption in the United States

In 1975, 44,286,000 metric tons[a] of phosphate rock were mined in 16 states in the United States, as shown in Figure 1 (3). Phosphate rock mined in Florida accounted for approximately 78% of the U.S. production and about 29% of the total world's supply in 1975. Over 92% of this output came from the vast sedimentary land pebble deposit in Polk and Hillsborough counties east of Tampa, Florida. Approximately 5.7% of the phosphate rock was mined in Tennessee and 3.6% in North Carolina. Deposits in Tennessee are classified as brown, white, and blue rock; only the brown rock has been of commercial importance. Phosphate rock mined in the western states of Idaho, Montana, Wyoming, and Utah accounts for about 14% of the total ore mined in the United States (3).

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[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented at the end of this report.

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(1) Riegel's Handbook of Industrial Chemistry, Seventh Edition. J. A. Kent, ed. Van Nostrand Reinhold Co., New York, New York, 1974. pp. 551-569.

(2) Handbook of Chemistry and Physics, 49th Edition, R. C. Weast, ed. The Chemical Rubber Co., Cleveland, Ohio, 1968. p. B-187.

(3) Stowasser, W. F. Phosphate-1977. Publication No. MCP-2, U.S. Department of the Interior, Bureau of Mines, Washington, D.C., May 1977. 18 pp.

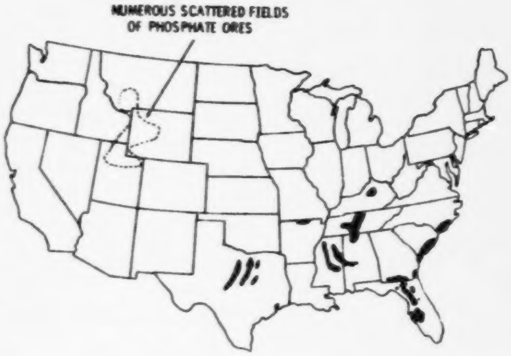

Figure 1. Location of major phosphate rock deposits in the United States (3).

Approximately 31,029,000 metric tons (70%) of the phosphate rock mined in 1975 were used in the United States to produce numerous phosphorus-containing materials (3). Figure 2 illustrates the 1975 consumption pattern for the various products obtained from phosphate rock. Significant quantities (15.9%) of phosphate rock were consumed in several nonagricultural markets such as the production of detergent builders and water treatment chemicals and the treatment of aluminum and ferrous metal surfaces, as well as in foods, beverages, pet foods, dentifrices, and fire control chemicals.

Agriculture-related industries producing phosphate fertilizers and animal feeds used 26,096,000 metric tons (84.1% of total production) of phosphate rock in 1975. Of this total, 22,754,000 metric tons (89.7%) were consumed for fertilizers, and 2,688,000 metric tons (10.3%) were used to produce animal feeds.

2. Types of Fertilizer Products

The schematic diagram of the phosphate fertilizer industry presented in Figure 3 (4) shows the conversion of insoluble phosphate ore into the soluble form necessary for plant consumption. Phosphate-bearing rock is mixed with sulfuric acid (H_2SO_4) to produce phosphoric acid, the building block for phosphate fertilizers.

As Figure 3 illustrates, numerous additional processes are used to produce phosphate fertilizer materials. These processes are in operation because of farmer demand for a wide variety of fertilizer mixtures.

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(4) Fullam, H. T., and B. P. Faulkner. Inorganic Fertilizer and Phosphate Mining Industries--Water Pollution and Control (PB 206 154). Grant 12020 FPD, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1971. 225 pp.

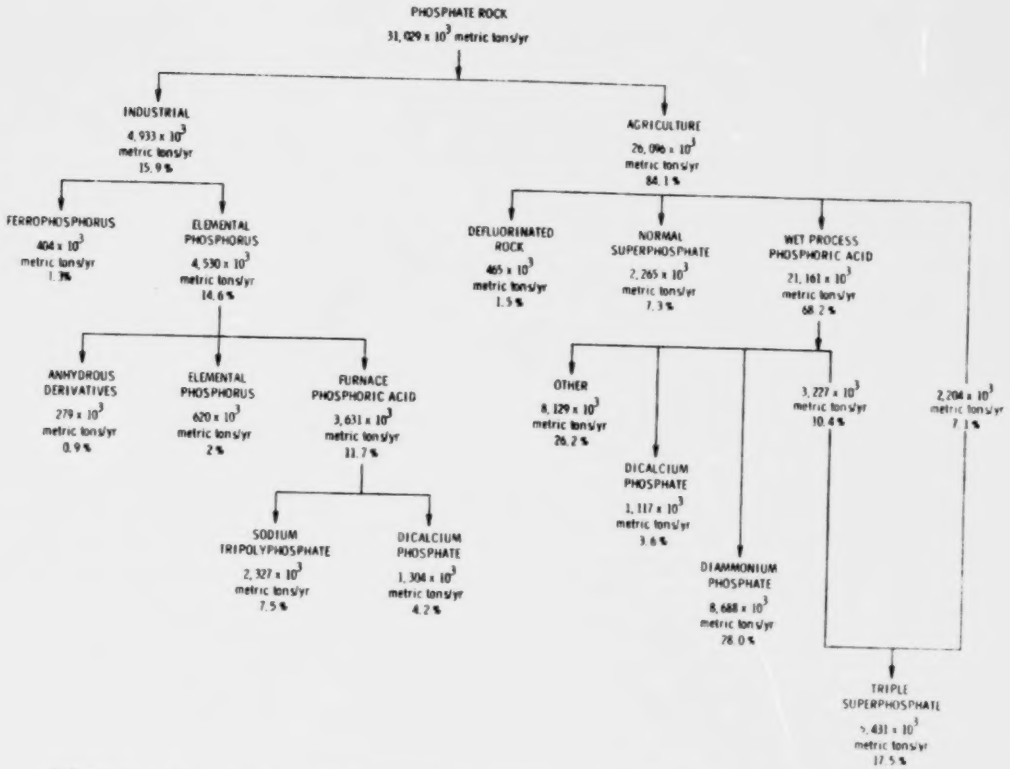
PHOSPHATE ROCK
31,029 x 10^3 metric tons/yr
INDUSTRIAL
4,933 x 10^3
metric tons/yr
15.9 %
AGRICULTURE
26,096 x 10^3
metric tons/yr
84.1 %
FERROPHOSPHORUS
404 x 10^3
metric tons/yr
1.3%
ELEMENTAL PHOSPHORUS
4,530 x 10^3
metric tons/yr
14.6 %
DEFLUORINATED ROCK
465 x 10^3
metric tons/yr
1.5 %
NORMAL SUPERPHOSPHATE
2,265 x 10^3
metric tons/yr
7.3 %
WET PROCESS PHOSPHORIC ACID
21,161 x 10^3
metric tons/yr
68.2 %
ANHYDROUS DERIVATIVES
279 x 10^3
metric tons/yr
0.9 %
ELEMENTAL PHOSPHORUS
620 x 10^3
metric tons/yr
2 %
FURNACE PHOSPHORIC ACID
3,631 x 10^3
metric tons/yr
11.7 %
OTHER
8,129 x 10^3
metric tons/yr
26.2 %
3,227 x 10^3
metric tons/yr
10.4 %
2,204 x 10^3
metric tons/yr
7.1 %
DICALCIUM PHOSPHATE
1,117 x 10^3
metric tons/yr
3.6 %
SODIUM TRIPOLYPHOSPHATE
2,327 x 10^3
metric tons/yr
7.5 %
DICALCIUM PHOSPHATE
1,304 x 10^3
metric tons/yr
4.2 %
DIAMMONIUM PHOSPHATE
8,688 x 10^3
metric tons/yr
28.0 %
TRIPLE SUPERPHOSPHATE
5,431 x 10^3
metric tons/yr
17.5 %

Figure 2. U.S. phosphate rock consumption pattern for various phosphorus products (3).

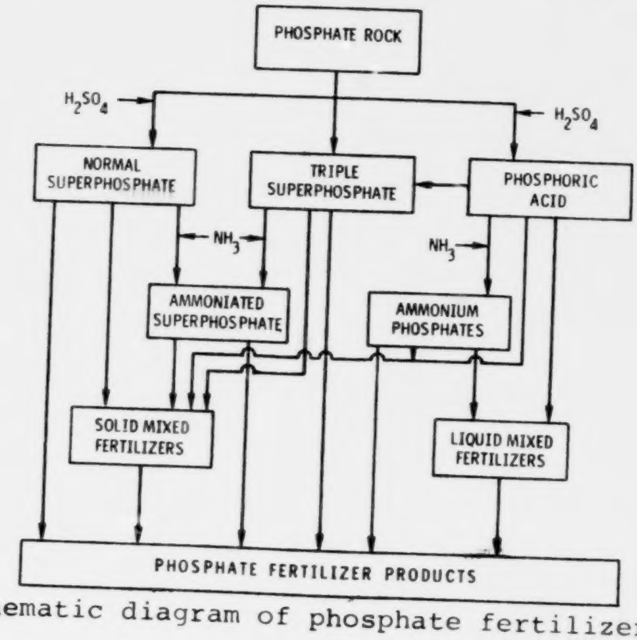
PHOSPHATE ROCK
H_2SO_4
H_2SO_4
NORMAL SUPERPHOSPHATE
TRIPLE SUPERPHOSPHATE
PHOSPHORIC ACID
NH_3
NH_3
AMMONIATED SUPERPHOSPHATE
AMMONIUM PHOSPHATES
SOLID MIXED FERTILIZERS
LIQUID MIXED FERTILIZERS
PHOSPHATE FERTILIZER PRODUCTS

Figure 3. Schematic diagram of phosphate fertilizer industry (4).

Product fertilizers differ in the amount and chemical form of the three primary plant nutrients: nitrogen (N), phosphorus (P), and potassium (K). Normal and triple superphosphate contain only one plant nutrient--phosphorus. Ammoniated superphosphate and ammonium phosphates contain two nutrients--phosphorus and nitrogen, while solid and liquid-mixed fertilizers contain all three nutrients in varying N-P-K ratios.

For evaluative purposes, the phosphate fertilizer industry is divided into three segments: phosphoric acid and superphosphoric acid, normal and triple superphosphate, and granular ammonium phosphate. Ammoniated superphosphates and solid and liquid-mixed fertilizer segments of the industry were covered in a separate Source Assessment Document on fertilizer mixing plants (5).

a. Phosphoric Acid and Superphosphoric Acid--
In 1975, 6,979,400 metric tons of phosphoric acid [reported as equivalent (100%) phosphorus pentoxide (P_2O_5)] were produced in the United States (6). Of this total, the 36 plants shown in Figure 4 (7) produced 90% or 6,291,400 metric tons from phosphate rock using wet process technology (3, 6). This report does not cover those plants which produce phosphoric acid from elemental phosphorus (thermal process) because this high purity acid is no longer used to produce phosphate fertilizers (8). The phosphate fertilizer industry consumed 86% or 5,380,648 metric tons of the wet process acid produced. The remainder (14%) of the wet process acid was used for preparing phosphatic feed supplements for livestock and poultry.

Phosphoric acid used in the fertilizer industry is made by the reaction of aqueous (50% to 98%) sulfuric acid with crushed phosphate rock, hence the term "wet process." The reaction occurs in an attack vessel where, in addition to phosphoric acid, insoluble calcium sulfate dihydrate (gypsum) and fluorine compounds are produced. Precipitated gypsum is filtered from the acid, sluiced with recycled pond water, and pumped to a gypsum pond. Fumes from the attack vessel are vented to a packed-bed wet scrubber for fluoride removal before they are exhausted to

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(5) Rawlings, G. D., and R. B. Reznik. Source Assessment: Fertilizer Mixing Plants. EPA-600/2-76-032c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 187 pp.

(6) Inorganic Chemicals 1976. M 28A(76)-14, U.S. Department of Commerce, Washington, D.C., August 1977. 30 pp.

(7) Hargett, N. World Fertilizer Capacity-Computer Printout. Tennessee Valley Authority, Muscle Shoals, Alabama, 1976.

(8) TVA Plans Early Closure of Furnaces; Cities Switch to Wet-Process Phosphoric. Chemical Marketing Reporter, 209(3), 1976.

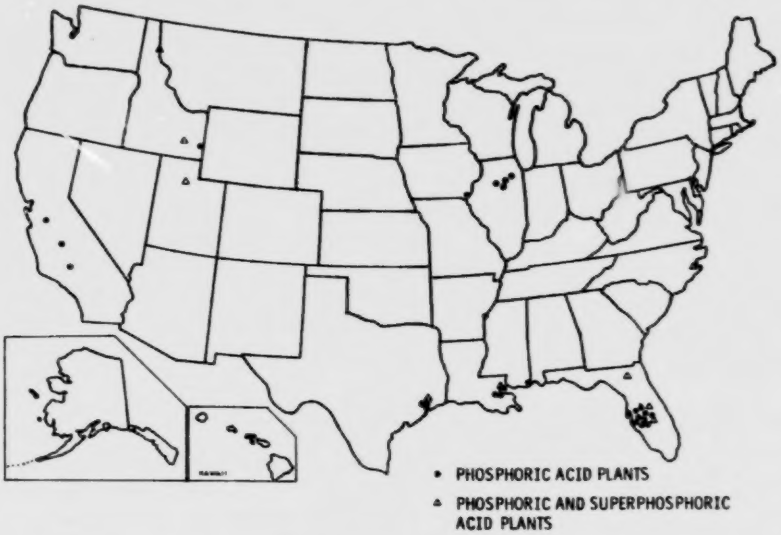

Figure 4. Location of wet process and superphosphoric acid plants (6).

the atmosphere. Low quality (28% to 30% P_2O_5 equivalent) phosphoric acid is then concentrated to 54% P_2O_5 equivalent by evaporating water from the solution.

Superphosphoric acid (P_2O_5 equivalent greater than or equal to 66%) is produced by further concentration of the 54% P_2O_5 phosphoric acid. Superphosphoric acid concentration is accomplished by either vacuum evaporation employing heat transfer surfaces or submerged combustion/direct heating. In 1975, approximately 505,900 metric tons of superphosphoric acid were produced by nine plants in six states in the United States, as shown in Figure 4 (6, 7) (Appendix A).

b. Normal and Triple Superphosphate--
Normal superphosphate (NSP), prepared by reacting ground phosphate rock with sulfuric acid, contains 16% to 22% available P_2O_5. Approximately 0.44×10^6 metric tons (P_2O_5 equivalent of NSP fertilizer were produced in 1975 (9).

Triple superphosphate (TSP), containing 45% to 55% available P_2O_5, is made by reacting ground phosphate rock with phosphoric acid. Two types of TSP are produced: run of the pile and granular. In 1975 approximately 0.60×10^6 metric tons (P_2O_5 equivalent), of run-of-the-pile triple superphosphate (ROP-TSP and

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(9) Inorganic Fertilizer Materials and Related Products. M28B(75)-13, U.S. Department of Commerce, Washington, D.C., December 1976. 6 pp.

0.90×10^6 metric tons of granular triple superphosphate (GTSP) were produced in the United States (9).

Geographical locations of the 66 NSP plants in the United States are shown in Figure 5 (7). NSP plants are located near consumers because it is cheaper to ship phosphate rock (approximately equal to 33% P_2O_5) to consumption areas than it is to ship NSP from the ore deposits. A description of each NSP plant is given in Appendix A.

The production of TSP, unlike that of NSP, occurs in plants located near phosphate rock deposits (Figure 6) (10). Eleven of the sixteen TSP plants are located in Florida, which accounts for approximately 78% of the U.S. production of phosphate-bearing rock. Among the 16 plants, 7 have facilities for producing both run-of-the-pile and granular grades of products; of the remaining 9 plants, 6 produce only GTSP and 3 produce only ROP-TSP (see Figure 6). Each of these plants is also described in Appendix A.

c. Ammonium Phosphate--
Ammonium phosphates are produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphate fertilizers are produced in the United States. In 1975, approximately 2.8×10^6 metric tons (P_2O_5 equivalent) of ammonium phosphates were produced by 48 plants located in 17 states, as shown in Figure 7 (7, 10, 11).

3. Raw Materials

Raw materials used in the phosphate fertilizer industry consist of phosphate rock, sulfuric acid, and anhydrous ammonia. Phosphate rock is a term broadly used to denote the group of minerals commercially valuable for their phosphorus content. The principal (greater than 80%) mineral constituent of phosphate rock is fluorapatite, $[Ca_3(PO_4)_2]_3 \cdot CaF_2$ (12). Also found in phosphate rock are iron oxides, aluminum oxides, magnesium, carbonates, carbon dioxide, calcium oxide, silicon oxides, and sulfates. A chemical analysis of phosphate rock samples from mines across the

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(10) Harre, E. A., M. N. Goodson, and J. D. Bridges. Fertilizer Trends 1976. Bulletin Y-111, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama, March 1977. 45 pp.

(11) Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants. EPA-450/2-77-005 (PB 265 062), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977. 277 pp.

(12) Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture. AP-57 (PB 192 222), U.S. Department of Health, Education, and Welfare, Raleigh, North Carolina, April 1970. 86 pp.

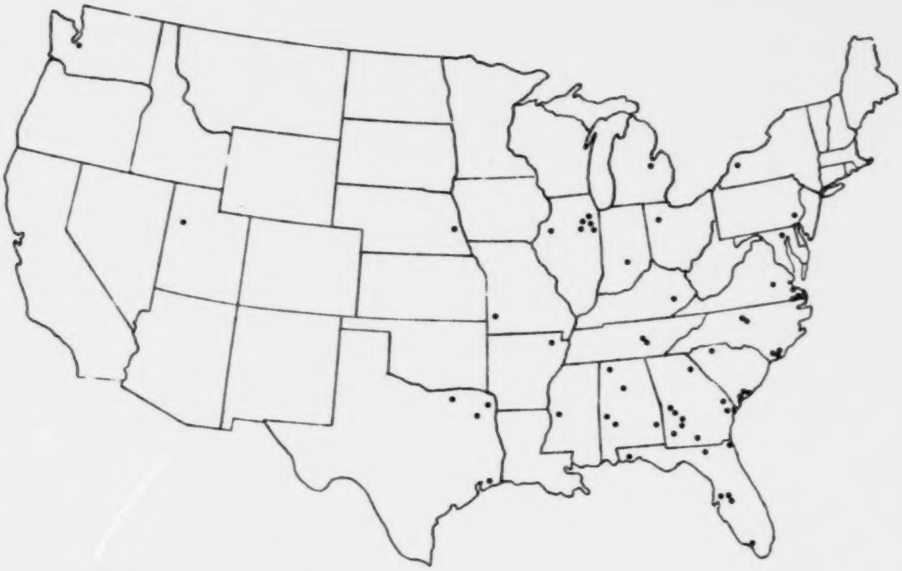

Figure 5. Location of NSP plants in the United States (7).

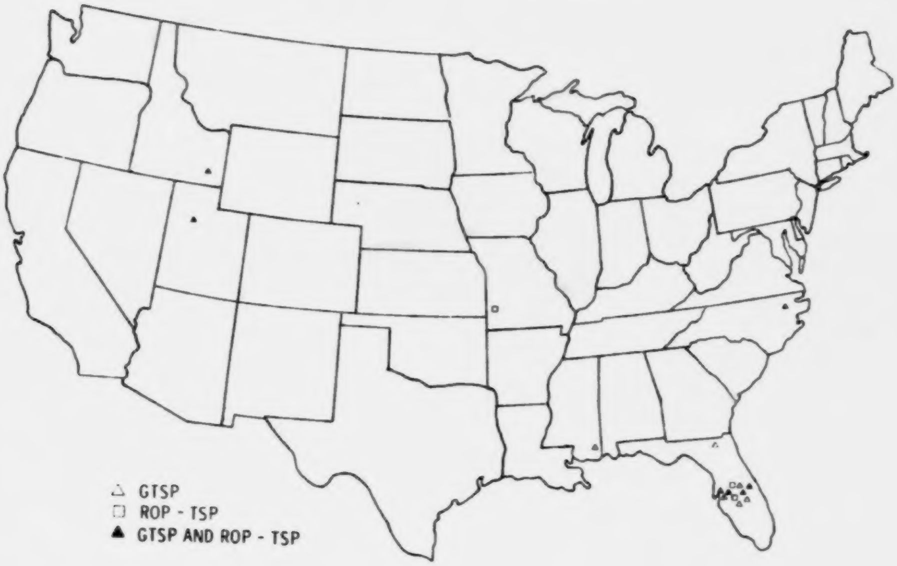
△ GTSP
□ ROP - TSP
▲ GTSP AND ROP - TSP

Figure 6. Location of TSP plants in the United States (10).

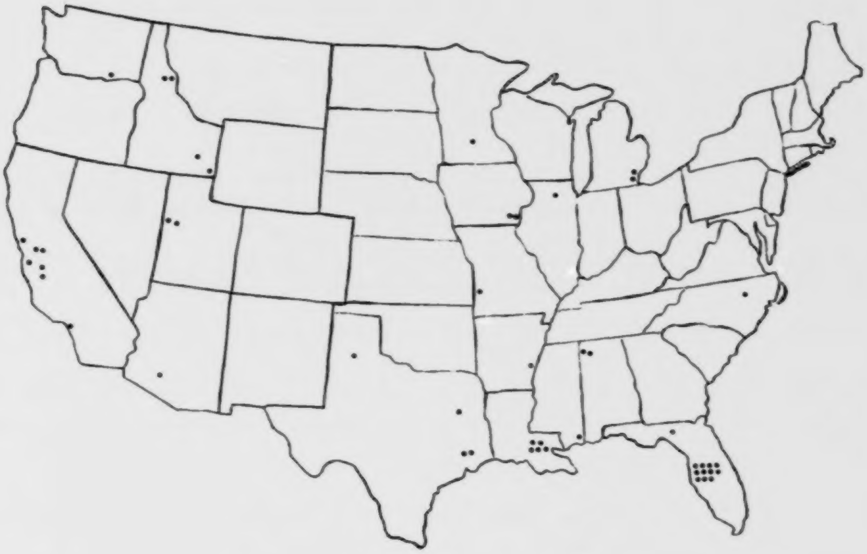

Figure 7. Location of ammonium phosphate plants in the United States (7, 10, 11).

United States is shown in Table 3 (13). Trace amounts of arsenic, lead, vanadium, and chromium which may be present in the rock are not listed. Uranium is also present in phosphate rock, with concentrations in the range of 40 g to 165 g of uranium per metric ton of rock. Table 4 (14) gives typical concentrations of radioactive elements in Florida phosphate mine products and wastes and phosphate fertilizer products and wastes.

Phosphorus content of the rock and/or products is commonly expressed in one of four ways:

- BPL [bone phosphate of lime or tricalcium phosphate, $Ca_3(PO_4)_2$].
- Phosphorus pentoxide (P_2O_5).
- Elemental phosphorus (P_4).
- Phosphoric acid (H_3PO_4).

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(13) Lowenheim, F. A. Phosphorus Compounds, Inorganic. In: Encyclopedia of Industrial Chemical Analysis, Volume 17, F. D. Snell and L. S. Ettre, eds. John Wiley & Sons, Inc., New York, New York, 1973. pp. 142-144.

(14) Guimond, F. J., and S. T. Windham. Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes. ORP/CSD-75-3, U.S. Environmental Protection Agency, Washington, D.C., August 1975. 30 pp.

TABLE 3. REPRESENTATIVE ANALYSES OF COMMERCIAL PHOSPHATE ROCKS (13)
(percent reported as material shown)

Reprinted from Encyclopedia of Industrial Chemical Analysis, Vol. 17, by courtesy of John Wiley & Sons, Inc.

U.S. location and type	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	SO_3	F	Cl	CO_2	Organic carbon	Na_2O	K_2O	H_2O[a]
Florida:														
Land pebble, high grade	35.5	48.8	0.04	0.9	0.7	6.4	2.4	4.0	0.01	1.7	0.3	0.07	0.09	1.8
Hard rock, high grade	35.3	50.2	0.03	1.2	0.9	4.3	0.1	3.8	0.005	2.8	0.3	0.4	0.3	2.0
Hard rock, waste pond	23.0	28.5	0.4	14.8	2.9	19.8	0.01	2.1	0.005	1.4	0.3	0.1	0.4	7.0
Tennessee:														
Brown rock, high grade	34.4	49.2	0.02	1.2	2.5	5.9	0.7	3.8	0.01	2.0	0.2	0.2	0.3	1.4
Western states:														
Phosphoric rock, high grade	32.2	46.0	0.2	1.0	0.8	7.5	1.7	3.4	0.02	2.1	1.8	0.5	0.4	2.5
Phosphoric rock, low grade	19.0	23.3	1.4	5.9	4.0	27.4	1.9	1.8	_[b]	4.0	5.0	1.5	1.0	3.5

[a] After drying at 100°C for several hours. [b] Data not available.

TABLE 4. RADIUM (^{226}Ra), URANIUM, AND THORIUM CONCENTRATIONS IN PHOSPHATE MINE PRODUCTS AND WASTES AND PHOSPHATE FERTILIZER PRODUCTS AND BYPRODUCTS (14)[a]
(pCi/g)[b]

Material	^{226}Ra	Uranium			Thorium			
		234	235	238	227	228	230	232
Marketable rock	42	41	1.9	41	2.0	0.61	42.3	0.44
Slimes	45	42	2.6	44	2.3	1.2	48	1.4
Sand tailings	7.5	5.2	0.38	5.3	-[c]			
Phosphoric acid	1.3							
Gypsum	33	6.2	0.32	6.0	0.97	1.4	13	0.27
Normal superphosphate	25							
Diammonium phosphate	5.6	63	3.0	63	1.6	0.8	65	0.4
Triple superphosphate	21	58	2.8	58	1.2	0.9	48	1.3
Monoammonium phosphate	5.0	55	2.9	55				
Sodium fluorosilicate	0.28							
Animal feed	5.5							

[a] Plants using Florida phosphate rock.
[b] Picocuries per gram; 1 picocurie equals 0.037 becquerel.
[c] Blanks indicate no data obtained.

Table 5 shows the factors required to convert from one set of units to another. The common industry practice of reporting all phosphorus-containing materials in terms of the equivalent phosphorus pentoxide (P_2O_5) content is used throughout the remainder of this document. Table 6 illustrates acid concentrations reported in various units.

Offsite preparation of phosphate rock involves beneficiation to remove impurities, drying to remove moisture, and grinding to improve reactivity.

TABLE 5. CONVERSION FACTORS FOR PHOSPHORUS CONTENT UNITS

To convert from	To	Multiply by
% BPL	% P	0.1997
% BPL	% P_2O_5	0.4576
% P_2O_5	% P	0.4364
% P_2O_5	% BPL	2.1853
% P_2O_5	% H_3PO_4	1.381
% H_3PO_4	% P	0.316
% H_3PO_4	% P_2O_5	0.724
% P	% P_2O_5	2.2914
% P	% BPL	5.0073

TABLE 6. COMMON CONCENTRATIONS OF PURIFIED PHOSPHORIC ACID GRADES (percent)

Material	H_3PO_4	P_2O_5	P	Polyphosphate
Filtered production phosphoric acid	28	20	9	0
	41	30	13	0
Orthophosphoric acid	75	54	24	0
Superphosphoric acid	97	70	31	2.2
	100	72	31	10

Sulfuric acid used in the wet process is either made in a captive plant or piped from a nearby sulfuric acid manufacturer. Virgin acid made from brimstone (native sulfur) or pyrites (sulfur bearing ores) is normally used. The use of byproduct sulfuric acid from other processes may introduce impurities that cause poor quality gypsum crystal formation and odor problems (15).

4. Rock Preparation

Phosphate rock that has been mined and beneficiated is in general too coarse to be used directly in acidulation. The major fraction of the phosphate rock (more than 98%) ranges in size from pebbles 25 mm in diameter down to 100-μm material (4). The rock is therefore processed through equipment to mechanically reduce it to the particle size needed for improved reactivity during the acidulation process (smaller than 150 μm).

Preliminary drying to remove moisture is necessary to prepare the rock for grinding (Figure 8). Direct-fired rotary kilns 8 m to 30 m long and 2 m to 3 m in diameter are used to dry phosphate rock (16). These dryers use natural gas or fuel oil as fuel and are fired countercurrently. In recent years, the fluidized-bed type of dryer has gained prominent importance because of its fuel savings and increased throughput.

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(15) Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. 1159 pp.

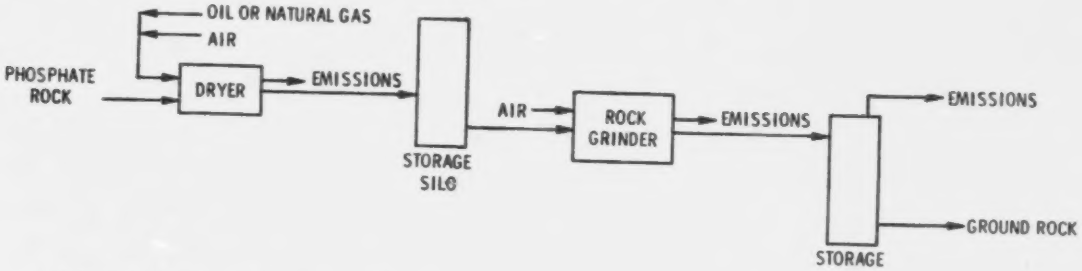

Figure 8. Preparation of phosphate rock for acidulation.

Size reduction is accomplished with ball, roll, or bowl mills. Rock is fed into the mills and mechanically ground to a fineness located between the particle size levels of 80% through a 150-μm and 95% through a 74-μm screen. After the rock enters the mill system, all flow through the sizing and reclamation circuits is by pneumatic means. Air is constantly exhausted from the mill system to prevent precipitation of moisture which is released from the rock during grinding.

Future rock grinding operations may utilize a wet grinding circuit rather than the current dry grinding practice. This change would eliminate the gas effluent streams associated with both rock drying and grinding operations and result in lower capital costs (17).

Phosphate rock arrives at the phosphate fertilizer plant in either a ground or unground form. For economic reasons, the trend has been toward more processing at the point where the rock is mined, especially at smaller plants (18).

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(16) Heller, A. N., S. T. Cuffe, and D. R. Goodwin. Inorganic Chemical Industry. In: Air Pollution, Volume III: Sources of Air Pollution and Their Control, A. C. Stern, ed. Academic Press, New York, New York, 1968. pp. 221-231.

(17) Martin, E. E. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Chemicals Segment of the Fertilizer Manufacturing Point Source Category. EPA-440/1-74-011-a (PB 238 652), U.S. Environmental Protection Agency, Washington, D.C., March 1974. 170 pp.

(18) Caro, J. H. Characterization of Superphosphate. In: Superphosphate: Its History, Chemistry, and Manufacture. U.S. Department of Agriculture, Washington, D.C., December 1964. pp. 272-284.

Ground rock requires tight, fully enclosed material handling equipment to reduce the loss of rock and prevent excessive air emissions. General shipping practice includes the use of enclosed, hopper-bottom railroad cars of the type developed for hauling cement and other finely ground material. Little (less than 5%) ground rock is carried by ship or barge because of handling losses that would be incurred.

In a typical system, ground rock is unloaded from the hopper-bottom cars into a receiving hopper located directly under the track. A vibrator is used to keep the rock flowing freely. An underground screw or belt conveyor carries the rock to storage silos. A typical rock unloading facility is shown in Figure 9. The unloading station, transfer conveyors, and storage silos are enclosed and all ventilation points are equipped with dust collectors.

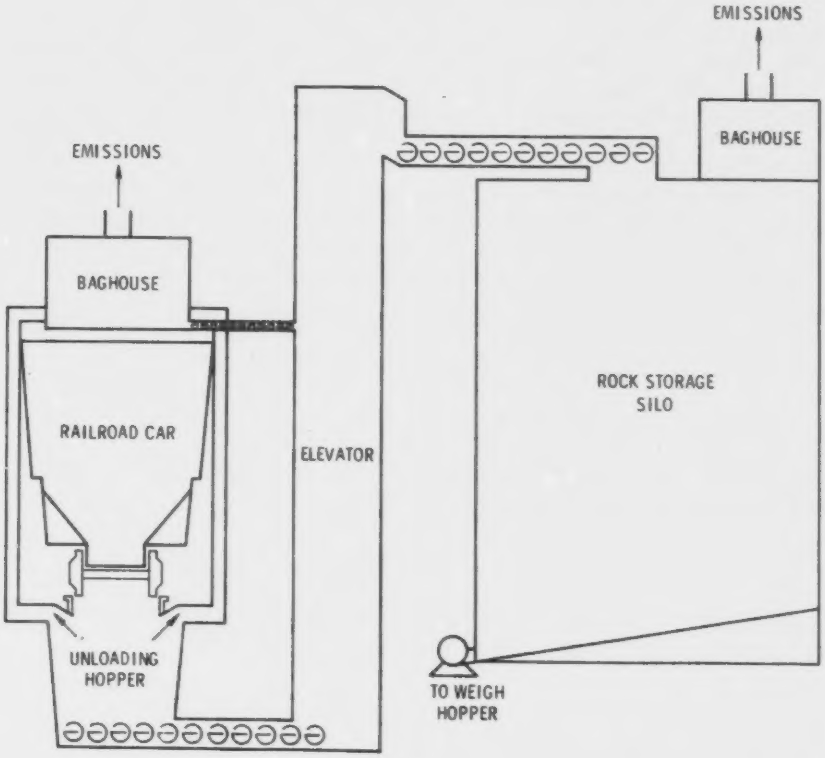
EMISSIONS
BAGHOUSE
EMISSIONS
BAGHOUSE
RAILROAD CAR
ELEVATOR
ROCK STORAGE SILO
UNLOADING HOPPER
TO WEIGH HOPPER

Figure 9. Raw material unloading and storage.

B. WET PROCESS PHOSPHORIC ACID PRODUCTION

1. Process Chemistry

In the wet process production of phosphoric acid, sulfuric acid and the tricalcium phosphate portion of the phosphate rock react to form phosphoric acid and gypsum (17).

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O) \qquad (2)$$

This chemistry is straightforward; however, two factors influence operating conditions at individual plants: the composition of the phosphate rock and the physical form of the byproduct calcium sulfate.

a. Effects of Phosphate Rock Composition--

Side reactions occur during acidulation, and the quantity of products found depends on the amounts and composition of other chemical constituents in the phosphate rock (see Table 3). These generally undesirable side reactions form precipitates and sludges which foul operating, handling, transfer, and storage equipment (19). Excessive amounts of impurities also increase acid viscosity, which affects handling operations. Metals such as iron, aluminum, and magnesium form water-insoluble phosphate salts, which tie up useful phosphate and remain as suspended solid impurities in product acids. Trace metals (arsenic, lead, and heavy metals) also contaminate the acid. Carbonates, fluorine, and silica likewise are troublesome materials (19). Carbonates react with sulfuric acid to produce carbon dioxide, which contributes to foaming. The calcium fluoride constituent of the fluorapatite ore reacts with sulfuric acid to produce hydrogen fluoride according to the following reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \qquad (3)$$

In addition, calcium fluoride reacts with phosphoric acid according to the following reaction (17, 20):

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF \qquad (4)$$

The hydrogen fluoride can evolve as a gas or react with silica in the following manner (17, 20):

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(19) Dahlgren, S. E. Chemistry of Wet-Process Phosphoric Acid Manufacture. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 91-154.

(20) Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry. Contract 68-02-1330, Task 3, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1976. 218 pp.

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (5)$$

During acid concentration steps, fluosilicic acid (H_2SiF_6) in the phosphoric acid solution can dissociate according to the following reaction (17, 20):

$$H_2SiF_6 \rightarrow SiF_4 + 2HF \quad (6)$$

Fluosilicic acid can also combine with sodium or potassium to yield fluosilicate salts, which form scale and sludge in the processing equipment.

b. Physical Form of Calcium Sulfate--
The popular process for phosphoric acid production is based on the quick formation of calcium sulfate dihydrate or gypsum ($CaSO_4 \cdot 2H_2O$). It is also possible to precipitate calcium sulfate as the hemihydrate ($CaSO_4 \cdot 1/2H_2O$) or the anhydrite ($CaSO_4$). The dihydrate processes offer basic advantages--less severe operating conditions, lower rates of corrosion, better filterability, and lower capital cost--which outweigh advantages in the hemihydrate and anhydrite processes. An alternative dihydrate process which does not involve direct formation of the dihydrate utilizes the initial formation of calcium sulfate in the hemihydrate form and its subsequent hydration to gypsum. Figure 10 (21) shows the precipitation of calcium sulfates in phosphoric acid.

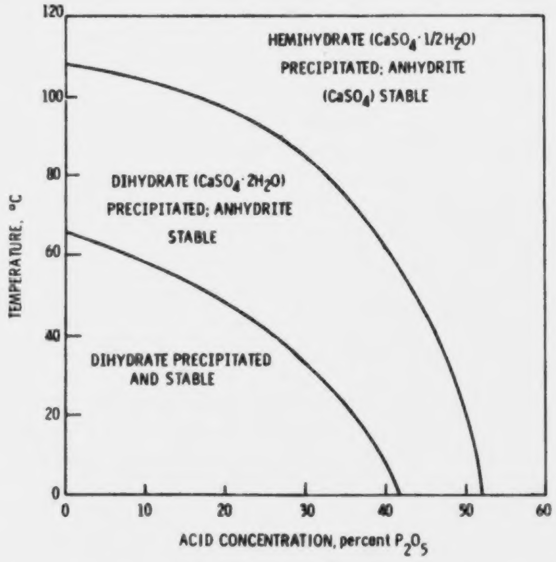

Figure 10. Precipitation and stability of calcium sulfates in phosphoric acid (21).

Reprinted from Chemistry and Technology of Fertilizers by courtesy of John Wiley & Sons, Inc.

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(21) Slack, A. V. Chemistry and Technology of Fertilizers. John Wiley & Sons, Inc., New York, New York, 1967. pp. 69-97.

The entire reaction, then, between the major (more than 90%) phosphate rock constituents and sulfuric acid is as follows (17):

$$Ca_{10}(PO_4)_6F_2CaCO_3 + 11H_2SO_4 + 11nH_2O$$
$$\longrightarrow 6H_3PO_4 + 11CaSO_4 \cdot nH_2O + 2HF + H_2O + CO_2 \qquad (7)$$

where n may equal 0, 1/2, or 2 depending on the degree of hydration of the calcium sulfate. Table 7 shows weight percent values of compounds found in filtered wet process phosphoric acid (WPPA) (22). Table 8 gives an elemental analysis of commercial (concentrated) acid (21).

2. Process Description

Phosphoric acid can be produced by one of two methods: hydration of phosphorus oxide derived from burning elemental phosphorus in air (thermal process) or digestion of phosphate rock with a mineral acid such as sulfuric acid (wet process). The acid produced by the thermal process is known as furnace grade acid and, by the nature of the process, is higher purity acid. Furnace grade acid, used for animal feeds, detergents, fire retardant chemicals, and other industrial phosphorus products, is no longer used to produce phosphate fertilizers (8).

The second, or wet process, method produces merchant grade phosphoric acid. Merchant grade acid contains more impurities than does furnace grade acid. Currently, all phosphate fertilizer production in the United States uses WPPA.

WPPA production methods differ principally in the degree of hydration of the calcium sulfate. The degree of hydration is a function of the temperature and phosphorus pentoxide concentration of the acidulation slurry (see Figure 10). Calcium sulfate can be precipitated in the dihydrate form (gypsum), hemihydrate form, or anhydrous form. Currently, all WPPA plants in the United States use the dihydrate process. The hemihydrate and anhydrite processes find limited use in Europe and Japan.

A schematic diagram of the basic dihydrate process for producing orthophosphoric acid by the wet process method is shown in Figure 11. Production of the acid involves four unit operations: raw material feed preparation, phosphate rock digestion, filtration, and concentration. The following sections contain detailed process descriptions of each of these four operations.

---

(22) Lehr, J. R. Purification of Wet Process Acid. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 637-686.

TABLE 7. TYPICAL COMPOSITION OF FILTERED WPPA (22, 23)
(weight percent)

Rock source	Acid composition										Composition of suspended solid
	P_2O_5	CaO	F	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3	
Florida[a]	27.3	0.15	1.7	0.6	1.1	0.28	0.03	0.08		1.2	A, B, C
[b]	28.4	0.1	1.5	1.1	2.0					3.9	
[b]	31.2	1.0	1.4	0.8	1.7					0.2	
[b]	26.3	0.4	2.0	0.5	1.1				1.1	1.0	
[b]	30.2	0.1	2.0	1.9	1.1				1.6	3.1	
[c]	30.0	1.26	2.36	1.08	0.86		0.06	0.01	1.21	3.72	
[c,d]	27.0 to 31.9	0.01 to 0.8	0.9 to 3.1	0.2 to 1.6	0.8 to 2.4				0.2 to 0.6	0.4 to 4.6	A, C
Western[a]	23.2	0.22	1.2	0.8	0.6	0.33	0.05	0.13		1.0	A, C
[c]	30.0	0.21	1.36	1.01	0.42	0.05	0.06	0.01	0.74	2.63	
Tennessee[c]	30.0	0.37	2.54	2.66	2.27		0.07	0.43	0.1	1.49	

[a] Composition of clear, supernatant acid after cessation of precipitation; compounds identified in solids: A = $CaSO_4 \cdot 2H_2O$, B = $Ca_4SO_4(AlF_6)(SiF_6)OH \cdot 12H_2O$, C = $(Na, K)_2SiF_6$.

[b] Compositions of acids include any suspended solid material in shipped acids.

[c] Data taken from Table II of Reference 23 and recalculated to 30% P_2O_5 basis for comparison.

[d] Composite analyses of 21 product acids.

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(23) Hill, W. L., H. L. Marshall, and K. D. Jacob. Composition of Crude Phosphoric Acid Prepared by Sulfuric Acid Process. Industrial and Engineering Chemistry, 24(9):1064-1068, 1932.

TABLE 8. TYPICAL COMPOSITION OF COMMERCIAL PHOSPHORIC ACID (21)
(weight percent)

Reprinted from Chemistry and Technology of Fertilizers by courtesy of John Wiley & Sons, Inc.

Component	Sample					Average
	A	B	C	D	E	
P_2O_5 equivalent	54.8	53.4	52.8	53.4	52.1	53.3
Calcium	0.01	0.01	0.05	0.1	0.03	0.06
Iron	0.7	0.8	0.7	1.2	0.5	0.78
Aluminum	0.7	0.3	0.4	0.6	0.6	0.52
Magnesium	0.3	0.2	0.3	0.3	0.2	0.26
Chromium	0.03	0.01	0.01	0.01	0.04	0.02
Vanadium	0.04	0.01	0.01	0.02	0.04	0.02
Sodium	0.03	1.9	0.04	0.2	0.1	0.45
Potassium	0.07	0.1	0.03	0.01	0.1	0.06
Fluoride	0.7	0.3	0.4	0.9	0.5	0.56
Sulfite	3.0	1.8	2.8	1.5	2.2	2.3
Silica	0.2	0.2	0.2	0.1	0.1	0.16
Carbon	0.1	0.04	0.8	0.2	0.04	0.24
Solid[b]	1.7	5.1	8.3	2.9	0.5	3.7

[a] Filtered WPPA is concentrated by evaporation to yield commercial acid.

[b] Filtered material, not washed, or dried.

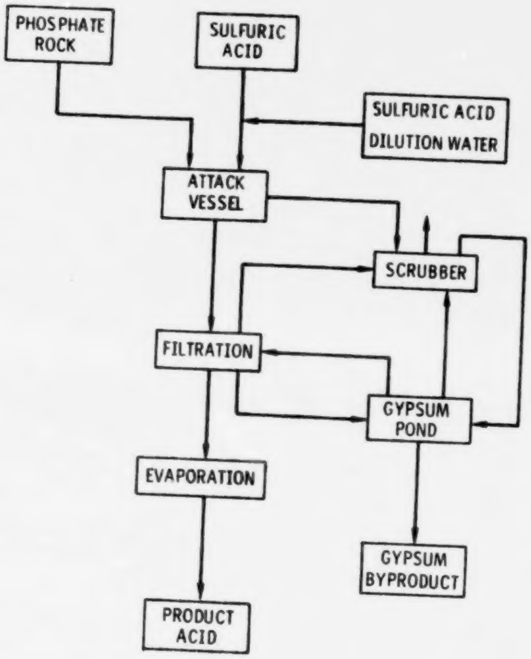
PHOSPHATE ROCK
SULFURIC ACID
SULFURIC ACID DILUTION WATER
ATTACK VESSEL
SCRUBBER
FILTRATION
GYPSUM POND
EVAPORATION
GYPSUM BYPRODUCT
PRODUCT ACID

Figure 11. Wet process for production of phosphoric acid.

a. Raw Material Feed Preparation--
Phosphate rock is delivered to the plant site by railroad hopper cars. Unloading of these cars takes place in a three-sided shed where the ore drops out of the bottom of the railroad car and is conveyed to rock storage silos.

An exhaust system is installed in the unloading and transfer areas to remove phosphate rock dust from the air. The exhaust stream is passed through a baghouse before it is discharged to the atmosphere. From the silos, the rock is classified by screening (60% to 80% less than 74 μm) or by air separation and is passed on to the acidulator.

In addition to phosphate rock, sulfuric acid (93% to 98% H_2SO_4) is delivered to the plant site. This acid is piped to storage tanks from adjacent sulfuric acid plants.

b. Phosphate Rock Digestion--
The key feature in a phosphoric acid plant is the acidulator, the reaction vessel where phosphate rock is digested with sulfuric acid to produce orthophosphoric acid (28% to 30% P_2O_5) and gypsum. Before the 1960's, the digestion section consisted of a series of separate reaction vessels. Today, all wet process acid plants use a single tank design consisting of multiple compartments or

stages (24). The types of acidulation systems currently in use in the United States include the Prayon, Prayon/Davy Powergas, Dorr-Oliver, Singmaster and Breyer, and Swenson.

Each system design varies in terms of the number and location of agitators and recirculation mechanisms and in the locations of rock and sulfuric acid injection points. In the United States, approximately 75% of all wet process acid trains use the Prayon or a combined Prayon/Dorr-Oliver system. As Figure 12 illustrates, each of the systems uses different equipment, but the basic process and resulting product and byproducts remain the same.

Phosphate rock and sulfuric acid are added to recirculating slurry in the acidulator. Approximately 3.35 metric tons of 70% BPL (32% P_2O_5) phosphate rock and 2.75 metric tons of 93% to 98% sulfuric acid are required to produce 1.0 metric ton of H_3PO_4 (100% P_2O_5 basis) (24). Some processes use dilute sulfuric acid; the range of concentrations is 50% to 98% sulfuric acid. The higher concentrations of sulfuric acid are generally preferred because they remove excess water that must be evaporated during the concentration step.

Average retention time in the reactor system ranges from 5.5 hr to 8 hr (21). In all systems, recirculation of slurry is required in order to reduce the adverse effects on the process caused by fluctuations in rock analysis and incomplete mixing. The recycled slurry also gives the control of supersaturation necessary for good growth of gypsum crystals. In multicompartment systems such as the Prayon single tank reactor, the recycle: product ratios range from 10:1 to 20:1 (24).

Acidulation of rock and dilution of sulfuric acid produce heat: 163 kJ to 469 kJ per mole of fluorapatite (19). The reaction slurry must be cooled to prevent formation of other hydrated crystal forms of calcium sulfate. Three methods of cooling are used: blowing air into the slurry, flowing air across the slurry, and vacuum flash cooling. Another approach, used by Prayon, is to apply sulfuric acid which is already diluted and cooled. When the heat of reaction and heat of dilution of sulfuric acid are removed by flash cooling (Figure 13), submerged slurry pumps lift the slurry from the attack tank and introduce it into the bottom of a distributor in the flash cooler. A large slurry surface in the top of the cooler flashes off water; the cooled slurry then overflows the inner and outer edges of the distributor and returns to the attack tank.

Vapors from the flash cooler are condensed in a barometric condenser and sent to a hot well. Noncondensables are removed by

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(24) Lutz, W. A., and C. J. Pratt. Principles of Design and Operation. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 158-208.

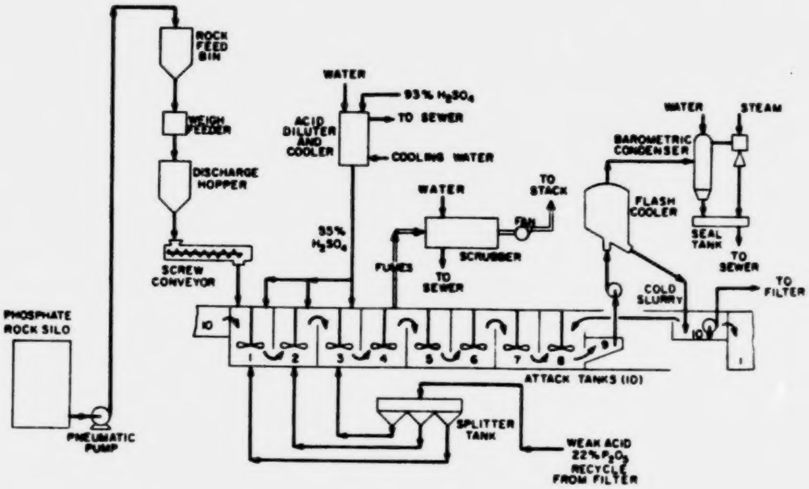
ROCK FEED BIN
WEIGH FEEDER
DISCHARGE HOPPER
SCREW CONVEYOR
PHOSPHATE ROCK SILO
PNEUMATIC PUMP
WATER
93% H_2SO_4
TO SEWER
ACID DILUTER AND COOLER
COOLING WATER
55% H_2SO_4
WATER
TO STACK
FAN
FUMES
SCRUBBER
TO SEWER
WATER
STEAM
BAROMETRIC CONDENSER
FLASH COOLER
SEAL TANK
TO SEWER
COLD SLURRY
TO FILTER
10
1
2
3
4
5
6
7
8
9
10
1
ATTACK TANKS (10)
SPLITTER TANK
WEAK ACID 22% P_2O_5 RECYCLE FROM FILTER

Figure 12a. Flow diagram for Prayon phosphoric acid plant.

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 254, by courtesy of Marcel Dekker, Inc.

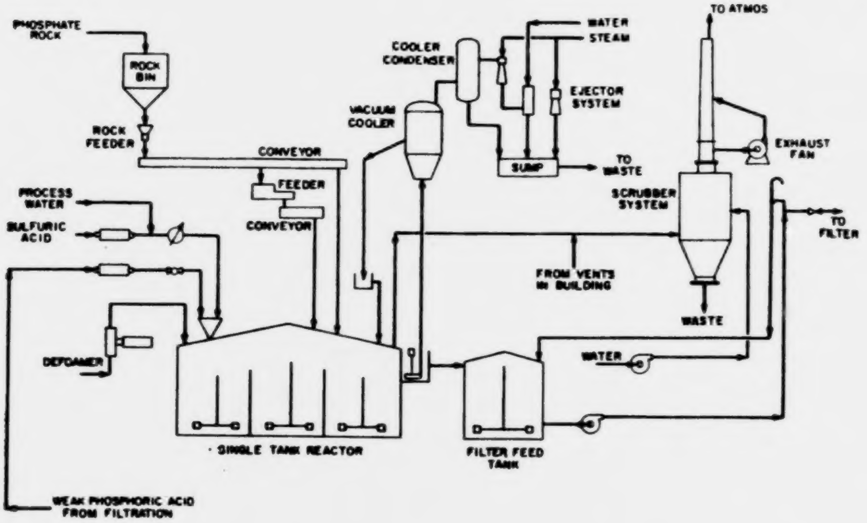
PHOSPHATE ROCK
ROCK BIN
ROCK FEEDER
CONVEYOR
FEEDER
CONVEYOR
PROCESS WATER
SULFURIC ACID
DEFOAMER
COOLER CONDENSER
WATER
STEAM
EJECTOR SYSTEM
VACUUM COOLER
SUMP
TO WASTE
TO ATMOS
EXHAUST FAN
SCRUBBER SYSTEM
TO FILTER
FROM VENTS IN BUILDING
WASTE
WATER
SINGLE TANK REACTOR
FILTER FEED TANK
WEAK PHOSPHORIC ACID FROM FILTRATION

Figure 12b. Dorr-Oliver reaction system (vacuum cooled).

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 216, by courtesy of Marcel Dekker, Inc.

Figure 12. Digestion system designs (24).

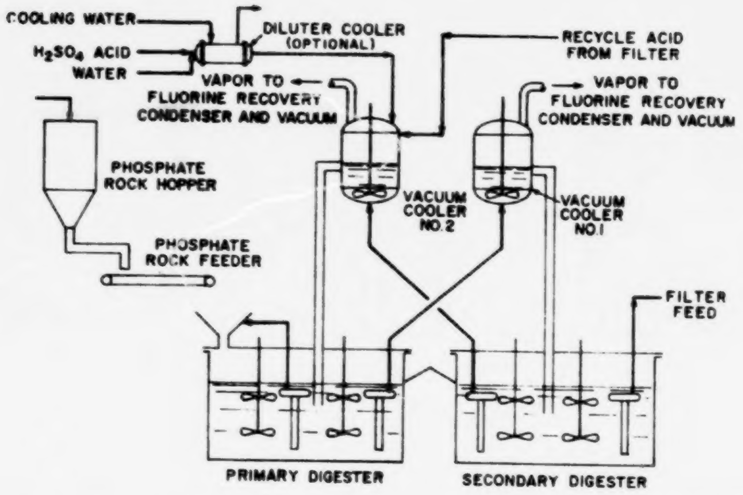
COOLING WATER
H₂SO₄ ACID
WATER
DILUTER COOLER (OPTIONAL)
RECYCLE ACID FROM FILTER
VAPOR TO FLUORINE RECOVERY CONDENSER AND VACUUM
VAPOR TO FLUORINE RECOVERY CONDENSER AND VACUUM
PHOSPHATE ROCK HOPPER
PHOSPHATE ROCK FEEDER
VACUUM COOLER NO.2
VACUUM COOLER NO.1
FILTER FEED
PRIMARY DIGESTER
SECONDARY DIGESTER

Figure 12c. Flow diagram for Singmaster and Bryer dihydrate phosphoric acid process.

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 274, by courtesy of Marcel Dekker, Inc.

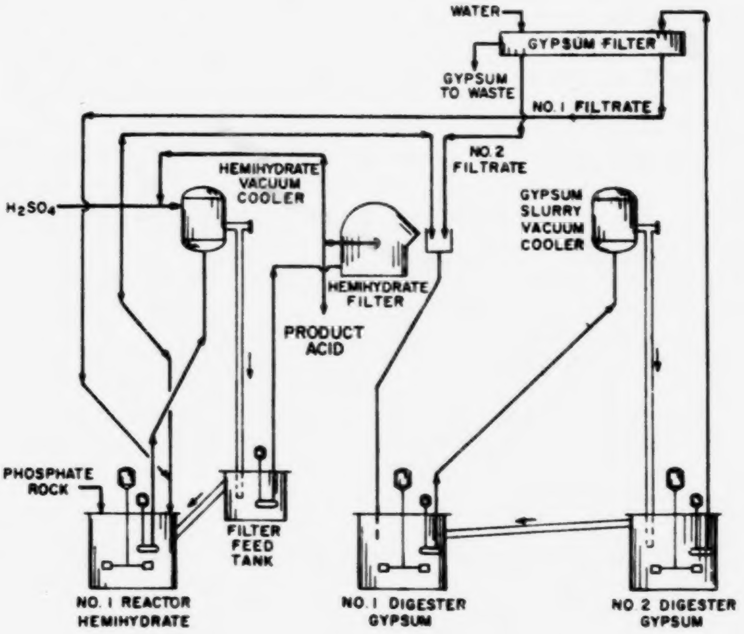
WATER
GYPSUM FILTER
GYPSUM TO WASTE
NO. 1 FILTRATE
NO. 2 FILTRATE
HEMIHYDRATE VACUUM COOLER
H_2SO_4
GYPSUM SLURRY VACUUM COOLER
HEMIHYDRATE FILTER
PRODUCT ACID
PHOSPHATE ROCK
FILTER FEED TANK
NO. 1 REACTOR HEMIHYDRATE
NO. 1 DIGESTER GYPSUM
NO 2 DIGESTER GYPSUM

Figure 12d. Flow diagram of Singmaster and Breyer hemihydrate-dihydrate process.

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 364, by courtesy of Marcel Dekker, Inc.

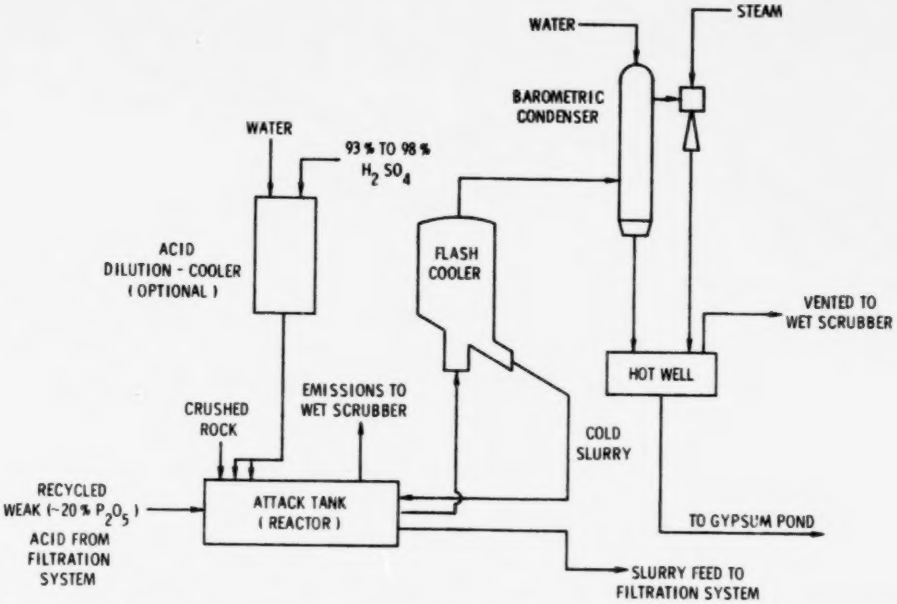
WATER
STEAM
BAROMETRIC CONDENSER
WATER
93 % TO 98 % H_2SO_4
ACID DILUTION - COOLER (OPTIONAL)
FLASH COOLER
VENTED TO WET SCRUBBER
HOT WELL
EMISSIONS TO WET SCRUBBER
CRUSHED ROCK
COLD SLURRY
RECYCLED WEAK (~20 % P_2O_5) ACID FROM FILTRATION SYSTEM
ATTACK TANK (REACTOR)
TO GYPSUM POND
SLURRY FEED TO FILTRATION SYSTEM

Figure 13. Phosphate rock digester and cooling system.

steam ejection and also vented to the hot well. Fumes from the hot well may be vented to the wet scrubber, while the water slurry is discharged to the gypsum pond.

c. Filtration--
Slurry from the final stage of the reactor system is continuously withdrawn and pumped to a horizontal, rotary, tilting pan type of vacuum filter to separate gypsum solids from the liquid (32% P_2O_5) phosphoric acid. Two diagrams of this type of filtration system are shown in Figures 14 (12) and 15 (15). Slurry is discharged onto the filter, the undiluted mother liquor is collected, and the remaining slurry is subsequently washed by three continuous, countercurrent stages to remove phosphoric acid liquids. The cake is dried by suction, the filter pan is inverted, and the cake is washed from the filter with recycled gypsum pond water. Gypsum slurry then flows to the holding pond for cooling and solid settling. The filter cloth is washed, dried by suction, and is then ready for the next cycle.

Acid from the first four stages of filtration is delivered to the vacuum receivers and then to a multicompartment filtrate seal tank. Undiluted mother liquor is pumped to a surge tank and then to the concentration process. Water and acid from the second and third washes are recycled to the preceding wash stage. Weak acid from the first wash is delivered to the attack vessel. Vapors from the vacuum receivers are cooled and vented to the wet scrubber system. Cooling water and condensed vapors are used to wash the cloth filter in the final stage of the filtration process.

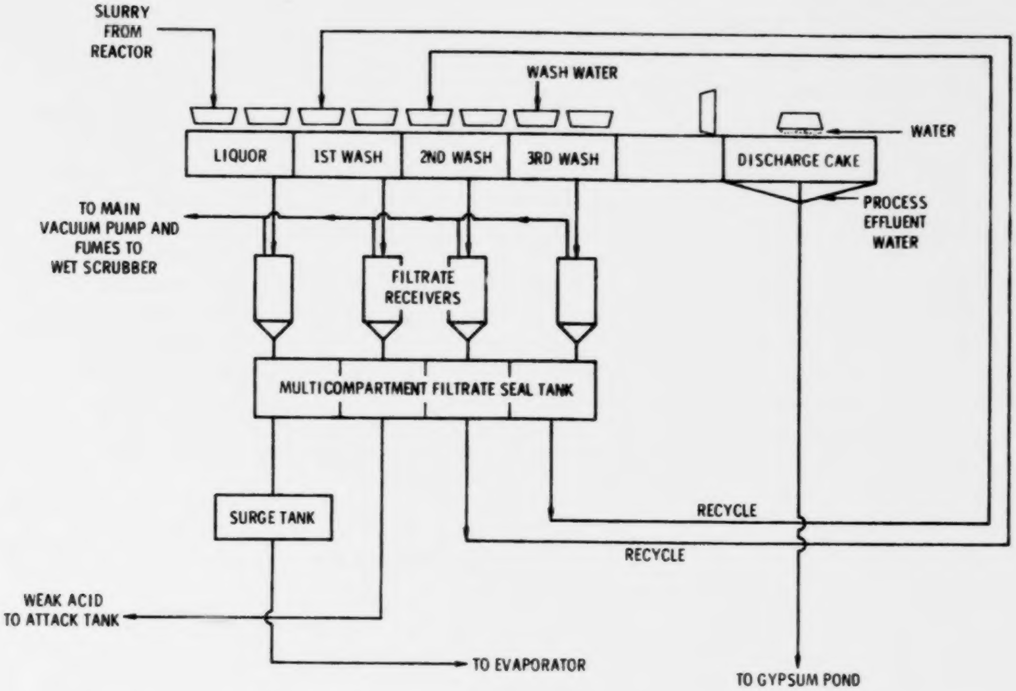
SLURRY
FROM
REACTOR
WASH WATER
WATER
LIQUOR
1ST WASH
2ND WASH
3RD WASH
DISCHARGE CAKE
TO MAIN
VACUUM PUMP AND
FUMES TO
WET SCRUBBER
PROCESS
EFFLUENT
WATER
FILTRATE
RECEIVERS
MULTICOMPARTMENT FILTRATE SEAL TANK
SURGE TANK
RECYCLE
RECYCLE
WEAK ACID
TO ATTACK TANK
TO EVAPORATOR
TO GYPSUM POND

Figure 14. Tilting pan filtration system (12).

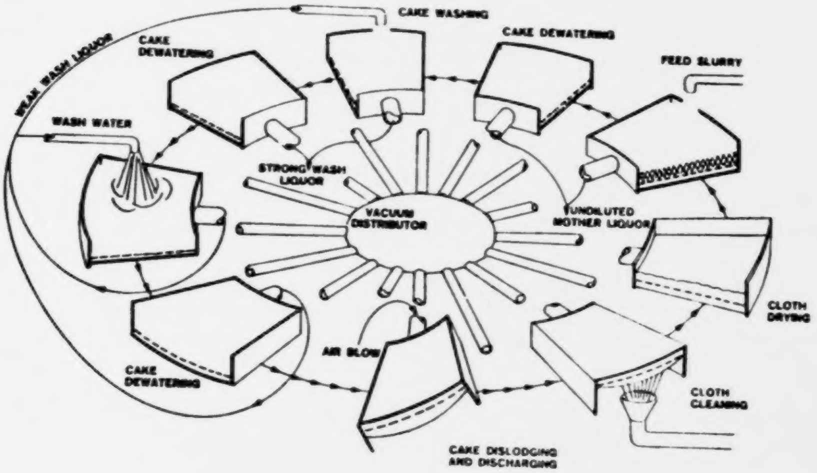
CAKE WASHING
CAKE DEWATERING
FEED SLURRY
WEAK WASH LIQUOR
CAKE
DEWATERING
WASH WATER
STRONG WASH
LIQUOR
VACUUM
DISTRIBUTOR
UNDILUTED
MOTHER LIQUOR
CLOTH
DRYING
AIR BLOW
CAKE
DEWATERING
CLOTH
CLEANING
CAKE DISLODGING
AND DISCHARGING

Figure 15. Operating cycle of rotary horizontal tilting pan filter (15).

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, p. 446, by courtesy of Marcel Dekker, Inc.

d. Concentration--

Phosphoric acid (32% P_2O_5) from the first filtration stage is concentrated to 54% P_2O_5 by vacuum evaporation of water. The acid is circulated, first through a shell-and-tube heat exchanger, then through a series of three flash chambers at 10 kPa to 20 kPa pressure (25, 26) separated by shell-and-tube exchangers, as shown in Figure 16 (12). The flash chambers serve to provide comparatively large liquid surface areas where water vapor can be released with minimum phosphoric acid entrainment.

Minor acid impurities, such as compounds containing fluorine, volatilize with the water vapor. The evolved vapors containing fluorine compounds and phosphoric acid pass to a barometric condenser, from which the condensed vapors, process cooling water, and condensed steam flow to a hot well. From the hot well, the water is recycled back to the barometric condenser that is used in connection with the acid flash cooler. Vapors from the hot well are vented to the wet scrubber system.

A variety of minor acid impurities such as iron and aluminum phosphates, soluble gypsum, and fluosilicates form supersaturated solutions in 54% P_2O_5 phosphoric acid and will precipitate during storage. These precipitates, in turn, cause problems in tank car unloading and customer processing. It is therefore necessary to remove these precipitated impurities before the acid is sold. As previously illustrated in Tables 7 and 8, there is a large reduction in impurities between the filtered and product acids.

The process used in the United States for removal of precipitated solids from 54% P_2O_5 phosphoric acid involves only physical treatment of the acid rather than the more complicated and expensive solvent extraction processes utilized in Europe and Mexico (27). Precipitated impurities are physically separated from the acid by settling and/or centrifugation.

Sludge is either sent to the gypsum pond, processed into a low quality fertilizer, or recycled to the evaporator feed tank. Recirculation of the sludge adds precipitated solids to the evaporator feed, providing crystal surfaces in the acid. Because salts coming out of solution during the evaporation process tend to deposit on these crystals rather than on evaporator surfaces, scaling is reduced. The clarified acid is then stored at ambient temperatures.

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(25) Cleanup Pays Off for Fertilizer Plant. Environmental Science and Technology, 6(5):400-401, 1972.

(26) Banford, C. R. IMC's New Plant Shows Off Latest H_3PO_4 Know-How. Chemical Engineering, 70(11):100-102, 1963.

(27) Legal, C. C., and O. D. Myrick, Jr. History and Status of Phosphoric Acid. In: Phosphoric Acid, Volume I., A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 1-89.

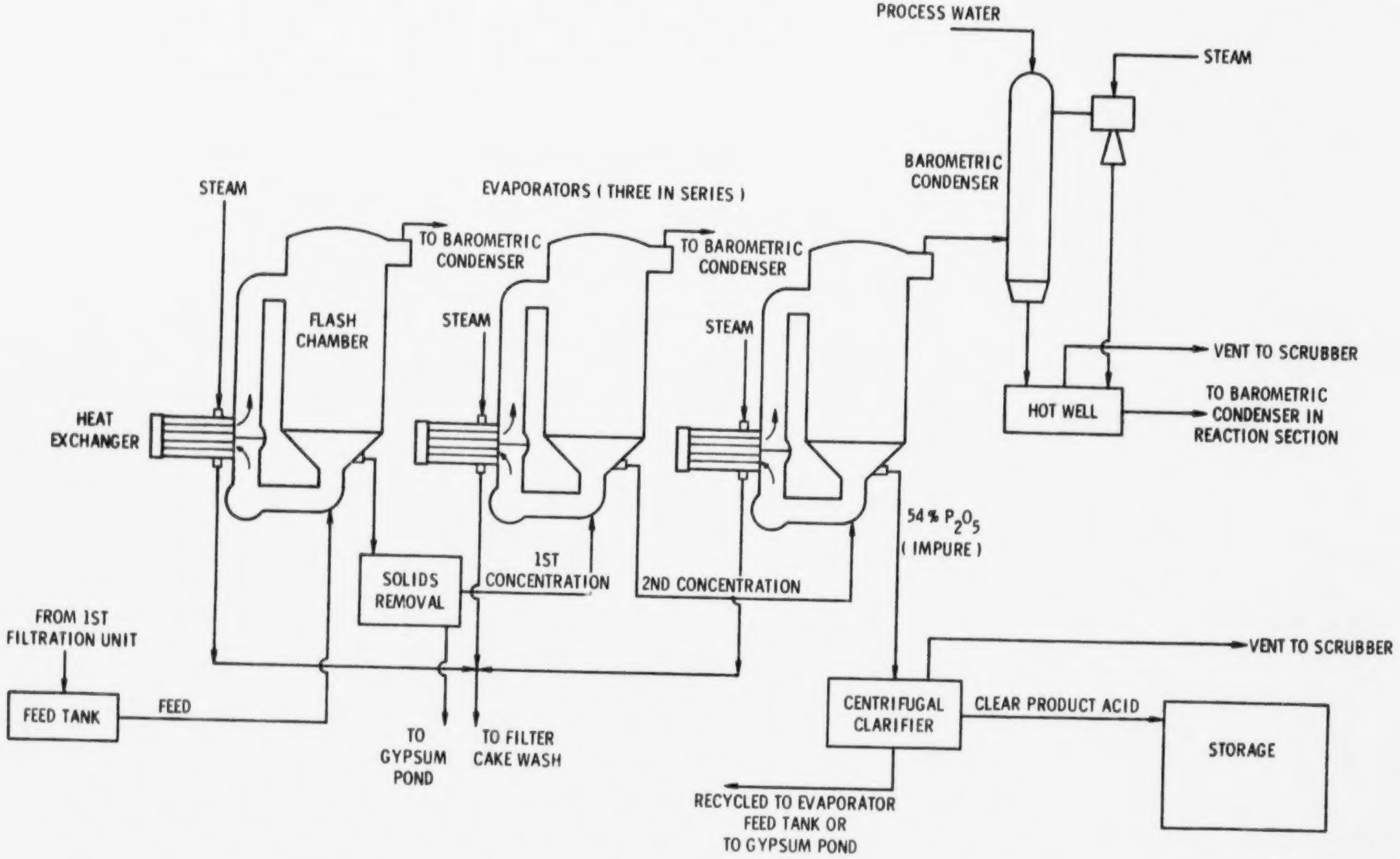
PROCESS WATER
STEAM
BAROMETRIC CONDENSER
STEAM
EVAPORATORS (THREE IN SERIES)
TO BAROMETRIC CONDENSER
TO BAROMETRIC CONDENSER
FLASH CHAMBER
STEAM
STEAM
VENT TO SCRUBBER
HEAT EXCHANGER
HOT WELL
TO BAROMETRIC CONDENSER IN REACTION SECTION
54 % P_2O_5 (IMPURE)
SOLIDS REMOVAL
1ST CONCENTRATION
2ND CONCENTRATION
FROM 1ST FILTRATION UNIT
VENT TO SCRUBBER
FEED TANK
FEED
CENTRIFUGAL CLARIFIER
CLEAR PRODUCT ACID
STORAGE
TO GYPSUM POND
TO FILTER CAKE WASH
RECYCLED TO EVAPORATOR FEED TANK OR TO GYPSUM POND

Figure 16. Concentration and clarification (12).

3. Gypsum Ponds

Gypsum ponds are used not only as settling basins for calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), but can be used as cooling, storage, and reconditioning ponds for all contaminated process water streams in the plant or complex. Cooled and clarified supernatant water from the pond can be recycled to supply over 80% of the water requirements for the plant (4).

A typical range of equilibrium compositions of gypsum pond water is given in Table 9 (4, 20, 28). Impurities approach equilibrium concentration in individual ponds over a period of 3 yr to 5 yr as the water is recycled. These concentrations are then maintained by either volatilization and/or precipitation.

TABLE 9. EQUILIBRIUM CONCENTRATION RANGES OF GYPSUM POND WATER (4,20, 28) (g/m^3)

Contaminant	Concentration
P_2O_5 equivalent	6,00 to 12,000
Fluoride	3,000 to 10,000
Sulfate	2,000 to 4,000
Calcium	350 to 1,200
Ammonia	0 to 100
Nitrate	0 to 100
Silica	~1,600
Aluminum	100 to 500
Iron	70 to 300
pH	1.0 to 1.8

4. Industry Characterization

All 36 WPPA plants in the United States (7) use the same basic processes described in previous sections. Specific equipment and operating conditions vary from plant to plant. General industry practice has included use of closed water recycle systems and a single scrubber unit for the collective emission sources, although variations do exist. One plant, located on the Mississippi River and lacking available land area for a gypsum pond, was designed for use of river water on a once through basis for scrubbing air emissions, for operation of the barometric condenser, and for meeting cooling requirements.

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(28) Huffstutler, K. K. Pollution Problems in Phosphoric Acid Production. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 727-739.

The 36 WPPA plants have production capacities which range from 6,480 to 751,300 metric tons of P_2O_5 per year, with an average plant capacity of 251,600 metric tons of P_2O_5 per year or 699 metric tons of P_2O_5 per day (see Appendix A). Individual plant capacities vary throughout the range as shown in Table 10 and illustrated in Figure 17. Average plant production was calculated by dividing the total annual wet process phosphoric acid production for 1975 (6,290,000 metric tons of P_2O_5 per year) by the total number of WPPA plants, i.e., 36. An average WPPA plant was therefore defined as producing 175,000 metric tons of P_2O_5 per year or 486 metric tons of P_2O_5 per day.

TABLE 10. DISTRIBUTION OF WPPA PLANTS BY PRODUCTION CAPACITY

Individual plant capacity, 10^3 metric tons P_2O_5/yr	Number of plants	Combined capacity for all plants in category, 10^3 metric tons P_2O_5/yr	Percent of total capacity
>700	1	751.3	8.3
600 to 700	3	2,023	22.3
500 to 600	2	1,187	13.1
400 to 500	3	1,358	15.0
300 to 400	1	326.5	3.6
200 to 300	7	1,720	19.0
100 to 200	9	1,297	14.3
<100	10	394.2	4.4
Total	36	9,057	100

Approximately 4 to 5 metric tons of gypsum are formed for every metric ton of P_2O_5 (20). The magnitude of this waste is an indication of the size of gypsum ponds, which also serve as holding ponds for the process water, necessary for plant operation. One reported rule of thumb for sizing is 0.00223 km² per daily metric ton of P_2O_5 production (20). An average plant, producing 486 metric tons P_2O_5 daily, would require a gypsum pond of 1.08 km² (263 acres).

The locations of the 36 phosphoric acid plants are listed in Table A-2 of Appendix A, which also gives information on the population densities in counties where the plants are located. A distribution of plants by county population density is shown in Table 11. The predominant population density range is 40 to 49 persons/km²; the median value for the 36 plants is 46.1 persons/km². This value is used for the population density around an average plant.

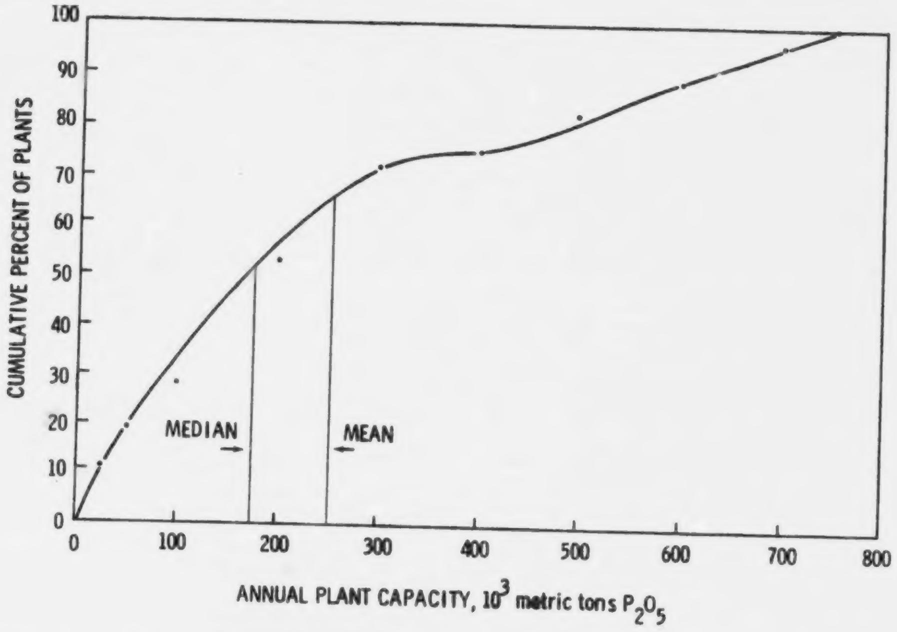

Figure 17. Distribution of WPPA plants by capacity.

TABLE 11. DISTRIBUTION OF WPPA PLANTS BY COUNTY POPULATION DENSITY

Population density, persons/km^2	Number of plants	Percent of total plants
0 to 9	4	11.1
10 to 19	5	13.9
20 to 29	2	5.6
30 to 39	4	11.1
40 to 49	14	38.9
50 to 99	1	2.8
100 to 299	3	8.3
300 to 500	3	8.3
Total	36	100

C. SUPERPHOSPHORIC ACID PRODUCTION

1. Process Chemistry

Superphosphoric acid is produced by dehydrating "wet process" phosphoric acid. When phosphoric acid is heated to elevated temperatures, molecular dehydration occurs and the molecules combine to form polyphosphoric acid chains as shown in Equation 8 (29).

$$x\ H_3PO_4 \xrightarrow{\Delta} H_{x+2}P_xO_{3x+1} + (x-1)H_2O \qquad (8)$$

As an example, tripolyphosphoric acid is formed as follows (29):

$$3H_3PO_4 \xrightarrow{\Delta} H_5P_3O_{10} + 2H_2O \qquad (9)$$

The resulting product is a mixture of phosphoric acid (H_3PO_4) and polyphosphoric acid chains of varying lengths; this mixture is called superphosphoric acid. If temperature or retention time is increased, a higher degree of dehydration is obtained. Product composition is affected in that the amount of phosphoric acid decreases while the average chain length of the polymeric acids increases. Wet process superphosphoric acid is concentrated to 68.5% to 72% P_2O_5 (27). At this degree of hydration, the P_2O_5 in the acid is approximately 40% remaining as phosphoric acid (H_3PO_4), 40% as pyrophosphoric acid ($H_4P_2O_5$), 5% as tripolyphosphoric acid, and 15% as longer chain acids (27).

Wet process superphosphoric acid differs from pure superphosphoric acid produced from electric-furnace phosphorus primarily in the chemistry associated with the impurities in the wet acid. Major impurities in wet process superphosphoric acid are calcium, iron, aluminum, magnesium, potassium, sodium, fluorine (hydrogen fluoride [HF], fluosilicic acid [H_2SiF_6], silicon tetrafluoride [SiF_4]), and sulfate (29). Minor amounts of chromium, tin, manganese, vanadium, uranium, and arsenic are also found. The composition of superphosphoric acid typically produced from Florida phosphate rock is shown in Table 12 (15).

Iron and aluminum impurities in wet process acid reach their lowest solubility at about 54% P_2O_5, the normal feed concentration to the superphosphoric acid process. In the product superphosphoric acid, pyrophosphoric acid acts to sequester trivalent iron and aluminum impurities and hold them in solution.

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(29) Muehlberg, P. E., J. T. Reding, and B. P. Shepherd. Draft Report: The Phosphate Rock and Basic Fertilizer Materials Industry. Contract 68-02-1329, Task 8, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1976. 205 pp.

TABLE 12. COMPOSITION OF SUPERPHOSPHORIC ACID (15)
(percent)

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 1083, by courtesy of Marcel Dekker, Inc.

Constituent	Typical content	Range
Total P_2O_5	69.60	69 to 70
Ortho-P_2O_5	42.50	42 to 45
Nonortho-P_2O_5	27.10	
Fe_2O_3	2.50	
Al_2O_3	2.05	
Combined Fe_2O_3 and Al_2O_3	4.55	4 to 5
Fluorine	0.51	
CaO	0.15	
SO_3	2.44	
Conversion to polyphosphate, %	29.0	

NOTE.—Blanks indicate data not available.

2. Process Description

a. Submerged Combustion--

Two commercial processes are used for the production of superphosphoric acid from wet process acid: submerged combustion and vacuum evaporation. Currently, in the United States only two plants (Allied Chemical Corp. and Occidental Petroleum Corp.), accounting for approximately 26% of the superphosphoric acid production capacity, use submerged combustion.

The submerged combustion process was pioneered by the Tennessee Valley Authority (TVA). Wet acid is dehydrated by bubbling hot combustion gases through a pool of the acid. Combustion gases are supplied by burning natural gas in a separate chamber. The combustion gases are diluted with air to maintain a gas temperature of 925°C for introduction into the acid evaporator. After passage through the acid, the hot combustion gases are sent to a separator to recover entrained acid droplets and then sent to a wet scrubber emissions control system.

Clarified acid containing 54% P_2O_5 is continuously fed to the evaporator from storage, and acid containing 72% P_2O_5 is withdrawn from the evaporator to product holding tanks. Acid cooling is accomplished by circulating water through stainless steel cooling tubes in the product tanks. Superphosphoric acid production can be controlled by regulation of the natural gas and air flows to the combustion chamber, by the feed rate of acid to the evaporator, or by the amount of excess air used in the combustion process.

b. Vacuum Evaporation--

Most plants in the United States (approximately 74%) employ vacuum evaporation utilizing heat transfer surfaces in the production of superphosphoric acid (15, 21). Two popular types of evaporators used are the falling film evaporator developed by Stauffer Chemical Co. and the forced circulation evaporator developed by Swenson Evaporator Co. In the seven plants which use vacuum evaporation, approximately 60% of superphosphoric acid production is by the Stauffer process. The remaining 40% uses the Swenson design.

In the Stauffer process, clarified 54% P_2O_5 phosphoric acid is continuously fed to the evaporator recycle tank where it mixes with superphosphoric acid from the evaporator. Some of the mixture (approximately 1.2%) is drawn off as product acid, but most (approximately 98.8%) is pumped to the top of the evaporator and is distributed across the heat exchanger tube bundle. The falling acid, heated by high-pressure steam condensing on the outside of the tubes, evaporates. The vapors and dehydrated acid then enter the separator section where entrained acid mist is removed. Product acid flows to the recycle tank, and the vapor is drawn off, condensed in a barometric condenser, and delivered to a hot well. Noncondensables are removed by a two-stage steam ejector and are vented to the hot well. Superphosphoric acid flows to the recycle tank where it is mixed with more 54% P_2O_5 phosphoric acid and recycled or removed as product. The approximate recycle to feed acid ratio is 80:1. The product stream is cooled and stored before shipping. Both the hot well and cooling tank are vented to wet scrubbing systems.

The Swenson process utilizes closed heat exchanger tubes filled with heat exchanger fluid to provide the heat of reaction. Feed acid (54% P_2O_5) pumped into the evaporating system mixes with recycled superphosphoric acid. As the acid leaves the exchanger tube bundle and enters the flash chamber, evaporation begins. Vapors are removed by a barometric condenser. Condensed materials and noncondensed vapors are delivered to a hot well. Product acid flows toward the bottom of the flash chamber where part (approximately 0.6%) is removed to a cooling tank and the rest (99.4%) is recycled. An approximate recycle to feed ratio is 150:1 (compared with 80:1 for the Stauffer process).

Cooling in both systems is accomplished by circulating water through stainless steel tubes in the holding tank.

3. Industry Characterization

Nine plants in the United States produce wet process superphosphoric acid. These plants have production capacities which range from 12,960 to 295,000 metric tons of P_2O_5 per year, with an average plant capacity of 115,900 metric tons of P_2O_5 per year or 320 metric tons of P_2O_5 per day (see Appendix A). Plant capacity distributions for those plants producing superphosphoric acid are given in Table 13 and Figure 18. Average plant production was calculated by dividing the total annual wet process superphosphoric and production for 1975 (506,000 metric tons of P_2O_5) by the total number of SPA plants. An average SPA plant was therefore defined as producing 56,200 metric tons of P_2O_5 per year or 156 metric tons per day.

TABLE 13. DISTRIBUTION OF SPA PLANTS BY PRODUCTION CAPACITY

Individual plant capacity, 10^3 metric tons P_2O_5/yr	Number of plants	Combined capacity for all plants in category, 10^3 metric tons P_2O_5/yr	Percent of total capacity
>200	1	295	28.3
150 to 200	3	479	45.9
100 to 150	1	124	11.9
50 t0 100	1	65.2	6.3
<50	3	79.6	
Total	9	1042.8	100

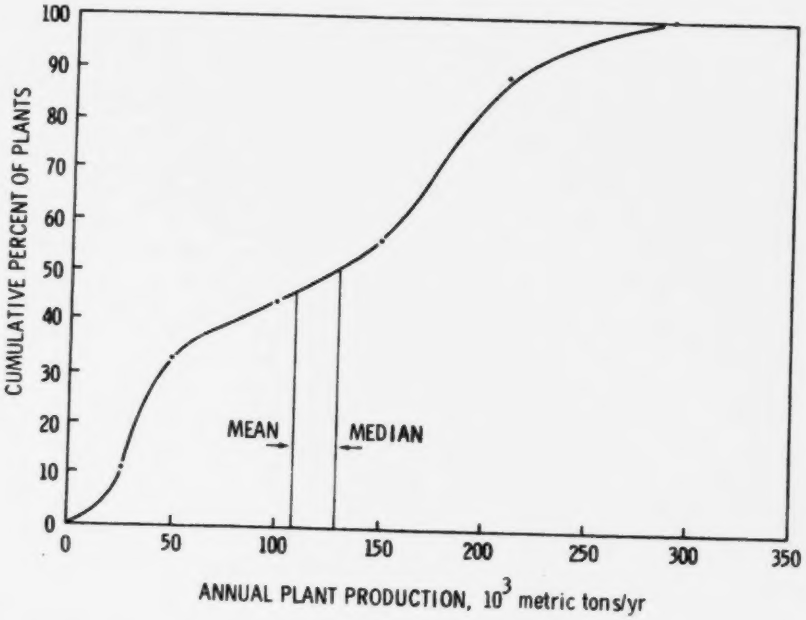

Figure 18. Distribution of SPA plants by capacity.

The population densities of the counties where the nine superphosphoric acid plants are located range from 2.9 to 385.9 persons/ km², is used for the population density around an average plant (Table 14).

TABLE 14. DISTRIBUTION OF SPA PLANTS BY COUNTY POPULATION DENSITY

Population density, persons/km²	Number of plants	Percent of total plants
0 to 9	2	22.2
10 to 19	2	22.2
20 to 39	0	
40 to 49	3	33.3
236	1	11.1
386	1	11.1
Total	9	100

D. NORMAL SUPERPHOSPHATE PRODUCTION

1. Process Chemistry

Phosphate rock is composed of phosphate in the form of the mineral fluorapatite $\{[Ca_3(PO_4)_2]_3 \bullet CaF_2\}$. Phosphate in this form is only slightly soluble in water, thus reducing its availability for plant growth.

NSP, containing from 16% to 21% P_2O_5, is prepared by reacting ground phosphate rock with 65% to 75% sulfuric acid. The primary objective of this acidulation process is to convert the fluorapatite in phosphate rock to soluble monocalcium phosphate, a form readily available to plants. While the overall chemistry is complex due to the composition of the rock, the major reaction involving phosphate may be stated simply as (4):

$$\underset{\substack{\text{Fluorapatite}\\\text{(phosphate rock)}}}{[Ca_3(PO_4)_2]_3 \cdot CaF_2} + \underset{\substack{\text{Sulfuric}\\\text{acid}}}{7H_2SO_4} + \underset{\text{Water}}{3H_2O} \longrightarrow \underset{\substack{\text{Monocalcium}\\\text{phosphate}\\\text{monohydrate}}}{3[CaH_4(PO_4)_2 \cdot H_2O]} + \underset{\substack{\text{Calcium}\\\text{sulfate}}}{7CaSO_4} + \underset{\substack{\text{Hydrogen}\\\text{fluoride}}}{2HF} \qquad (10)$$

2. Process Description

NSP is prepared by reacting ground phosphate rock with 65% to 75% sulfuric acid. Rock and acid are mixed in a reaction vessel, held in an enclosed area (den) while the reaction mixture solidifies, and then transferred to a storage pile for curing. A generalized flow diagram of the process for the production of NSP is shown in Figure 19 (4).

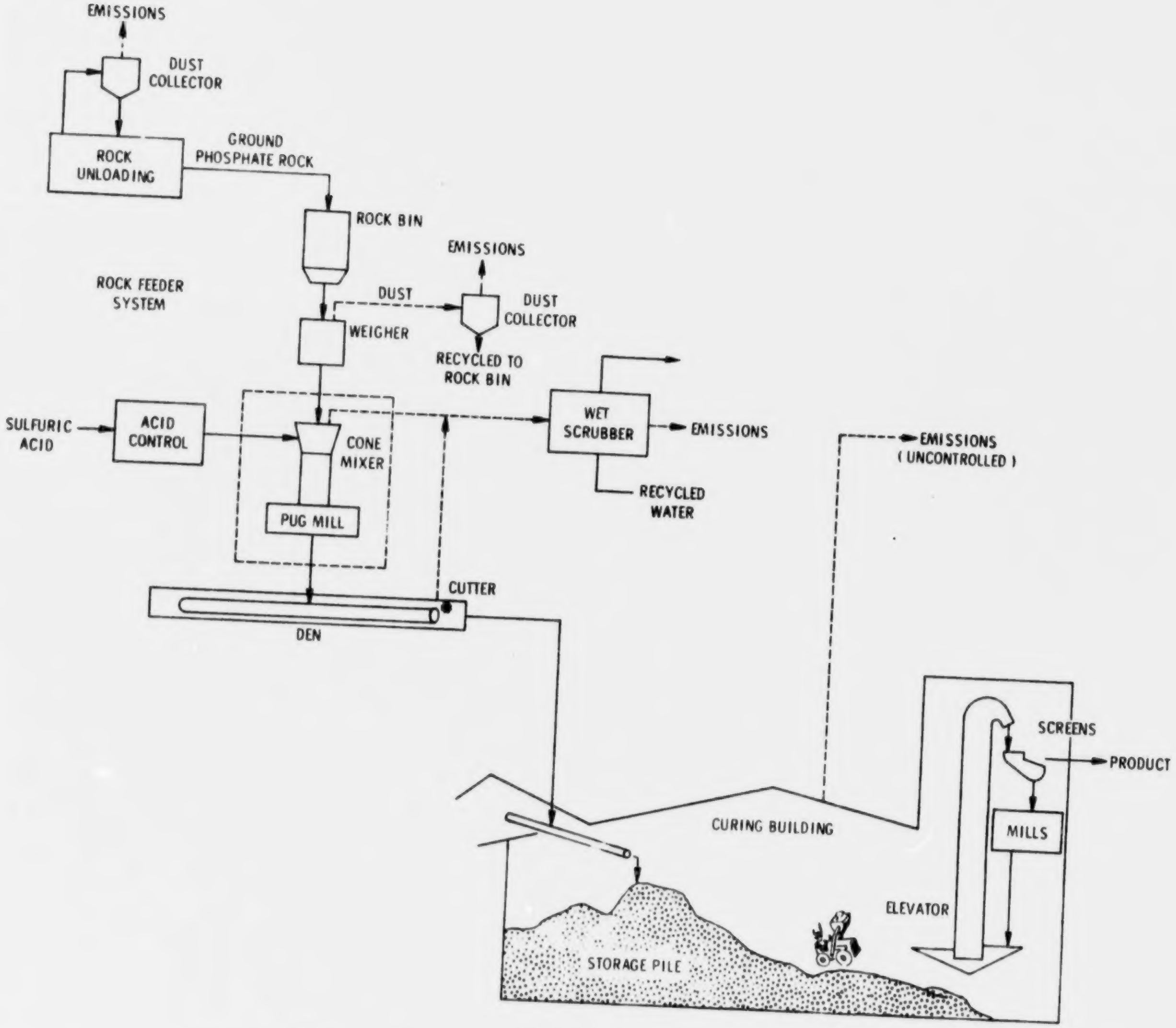
EMISSIONS
DUST COLLECTOR
ROCK UNLOADING
GROUND PHOSPHATE ROCK
ROCK BIN
ROCK FEEDER SYSTEM
EMISSIONS
DUST
DUST COLLECTOR
WEIGHER
RECYCLED TO ROCK BIN
SULFURIC ACID
ACID CONTROL
CONE MIXER
PUG MILL
WET SCRUBBER
EMISSIONS
RECYCLED WATER
EMISSIONS (UNCONTROLLED)
CUTTER
DEN
SCREENS
PRODUCT
CURING BUILDING
MILLS
ELEVATOR
STORAGE PILE

Figure 19. ROP-NSP production facility (4).

Mixing of the phosphate rock and sulfuric acid (acidulation) takes place in either a pan or cone mixer. The pan mixer, used in conjunction with a batch den and largely replaced by the cone mixer, is fitted with slowly rotating plows. Larger units are capable of handling a 2-metric ton batch of material (16).

The cone mixer, developed by the TVA, has come into use in more than 80% of the plants because of its relatively low capital expense, low maintenance cost, simple operation, and lack of moving parts (16). Sulfuric acid is fed into the cone tangentially in order to provide the necessary mixing action. Fresh superphosphate discharges from the cone mixer to a pugmill for additional mixing of acid and rock before discharge to a den. This type of mixer is suitable for use with either a batch or continuous den.

Plants are described as batch or continuous, depending upon the type of den used. In a continuous den, solidification and concurrent evolution of reaction gas take place on a slow-moving conveyor (den) enroute to the curing area. The low travel speed allows about 1 hr for the solidification process to occur before the material reaches the end of the belt. A cutting knife then slices the solidified material from the belt. NSP as it comes from the den is uncured and must be held in a curing building for a period of between 2 wk and 6 wk to permit acidulation to go to completion.

A batch den is a closed compartment except for a vent that releases reaction gases. Batch dens commonly used in this country have capacities ranging from 35 to 275 metric tons (16). After a setting period, ranging from 1.5 hr up to 10 hr, the solidified NSP material must be removed from the den and transferred to storage. Dens operate either automatically, with a cutting wheel that shaves the solidified mass from the den, or manually, with a mechanical cutter, a drag line, or a crane.

Following curing, the product can be ground and bagged for sale, or it can be granulated for sale as granulated superphosphate or granular mixed fertilizer. Granular mixed fertilizers are described in a separate report entitled "Source Assessment: Fertilizer Mixing Plants" and are therefore not included in the present discussion (5).

In producing a granular normal superphosphate (GNSP) material, the hardened ROP product is first fed to a pulverizer where it is crushed, ground, and screened. Screened material is then sent to a rotary drum granulator. Steam or water is added, if needed, to aid in granulation. The mixture then passes through a rotary dryer where it is dried to set its form and sufficient moisture is removed to eliminate the chance of the pellets binding together. The material then goes through a rotary cooler and on to storage bins for sale as bagged or bulk product.

In some cases, the ROP-NSP material is granulated before curing in a similar operation.

Sources of emissions at an NSP plant include the mixer, den, and curing building. Emissions of fluoride and particulate from the mixer and den are controlled by scrubbing with recycled water. Fluorides evolved during curing and particulates released from fertilizer handling operations (including screening and milling in the product storage building) are uncontrolled at a typical plant. The ground rock unloading, transfer, and storage facilities together with the process rock weighers and feeders comprise an additional source of particulate emissions. These emissions are controlled by baghouse collectors.

3. Industry Characterization

Only a small portion (less than 10%) of total NSP production is applied directly as ROP-NSP or GNSP product (30). GNSP accounts for less than 5% of total NSP production, and emissions from this plant type are therefore not considered. Most of the NSP material is sent to a fertilizer mixing plant and used in the preparation of fertilizers containing more than one of the following nutrients: nitrogen, phosphorus, and potassium.

An average NSP plant is defined as one that produces 6,650 metric tons of P_2O_5 per year of run-of-the-pile grade fertilizer. The average NSP plant is located in a county having a population density of 426 persons/km². (See Appendix A for a complete list of plant capacities and locations.) Because individual plant production statistics are not available, the average plant production rate was calculated by dividing the total annual NSP production for 1975 (439,000 metric tons P_2O_5 per year) by the total number of NSP plants; i.e., 66.

E. TRIPLE SUPERPHOSPHATE PRODUCTION

1. Process Chemistry

TSP, 45% to 49% P_2O_5, contains between 2.5 and 3 times more P_2O_5 than normal superphosphate. This higher P_2O_5 content product is achieved through the use of phosphoric acid in place of sulfuric acid as shown in the following equation (31):

$$\underset{\substack{\text{Fluorapatite}\\\text{(phosphate rock)}}}{[Ca_3(PO_4)_2]_3\cdot CaF_2} + \underset{\substack{\text{Phosphoric}\\\text{acid}}}{14H_3PO_4} + \underset{\text{Water}}{10H_2O} \longrightarrow \underset{\substack{\text{Monocalcium}\\\text{phosphate}\\\text{monohydrate}}}{10[CaH_4(PO_4)_2\cdot H_2O]} + \underset{\substack{\text{Hydrogen}\\\text{fluoride}}}{2HF} \qquad (11)$$

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(30) Personal communication with Ed Harre, Tennessee Valley Authority, Muscle Shoals, Alabama, 14 April 1977.

(31) Background Information for Standards of Performance: Phosphate Fertilizer Industry, Vol. 1--Proposed Standards. EPA-450/2-74-019a (PB 237 606), U.S. Environmental Protection Agency, Raleigh, North Carolina, October 1974. 140 pp.

Higher grade TSP materials (with 54% to 55% P_2O_5) have been manufactured by the TVA but only on an experimental basis (9, 32).

2. Process Description

Two principal types of TSP are produced: ROP-TSP and GTSP. Physical characteristics and processing conditions differ for the two materials. ROP material is essentially a nonuniform pulverized mass. In contrast, GTSP is a hard, uniform, pelletized granule. The ROP process is used for approximately 40% of total TSP production, and the granular process is used for the remaining 60%. Some overlap occurs as a portion of the ROP product is consumed in producing a GTSP product.

a. Run-of-Pile Triple Superphosphate--

The ROP-TSP production process as shown in Figure 20 is essentially identical to the NSP process except that phosphoric acid rather than sulfuric acid is used for acidulation (31). Mixing of the ground rock and phosphoric acid (50% to 54% P_2O_5 content) occurs in a cone mixer. The majority of plants (more than 90%) in the United States use the TVA cone mixer. This mixer has no moving parts, and mixing is accomplished by the swirling action of rock and acid streams introduced simultaneously into the cone. The resulting viscous slurry, on discharge from the mixer, quickly (in 15 s to 30 s) becomes plastic and begins to solidify. Solidification, together with the concurrent evolution of reaction gases, takes place on a slow-moving conveyor (den) enroute to the curing area.

On its way to the curing building, the mix may pass through several mixers or plungers that increase contact between the rock and acid and help to release trapped gases. Solidified material takes on a honeycomb appearance because of the copious evolution of gas throughout the mass. At the point of discharge from the den, the material passes through a rotary mechanical cutter that breaks up the solid mass. Coarse ROP product is sent to a storage pile where it is cured for a period of 3 wk to 5 wk. Final ROP product is then mined from the "pile" in the curing shed, and subsequently crushed, screened, and shipped in bulk (4, 16, 31).

This method of production gives a material that is nonuniform in particle size with consequent inferior handling characteristics. As a result, over 90% of all ROP-TSP is later granulated, either by the process described in the next section, or at fertilizer mixing plants that produce nitrogen-phosphorus-potassium (N-P-K) fertilizers (5). The remaining ROP-TSP is used as direct application fertilizer. Sources of air emissions and emission species

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(32) Gartrell, F. E., and J. C. Barber. Pollution Control Interrelationships. Chemical Engineering Progress, 62(10); 44-47, 1966.

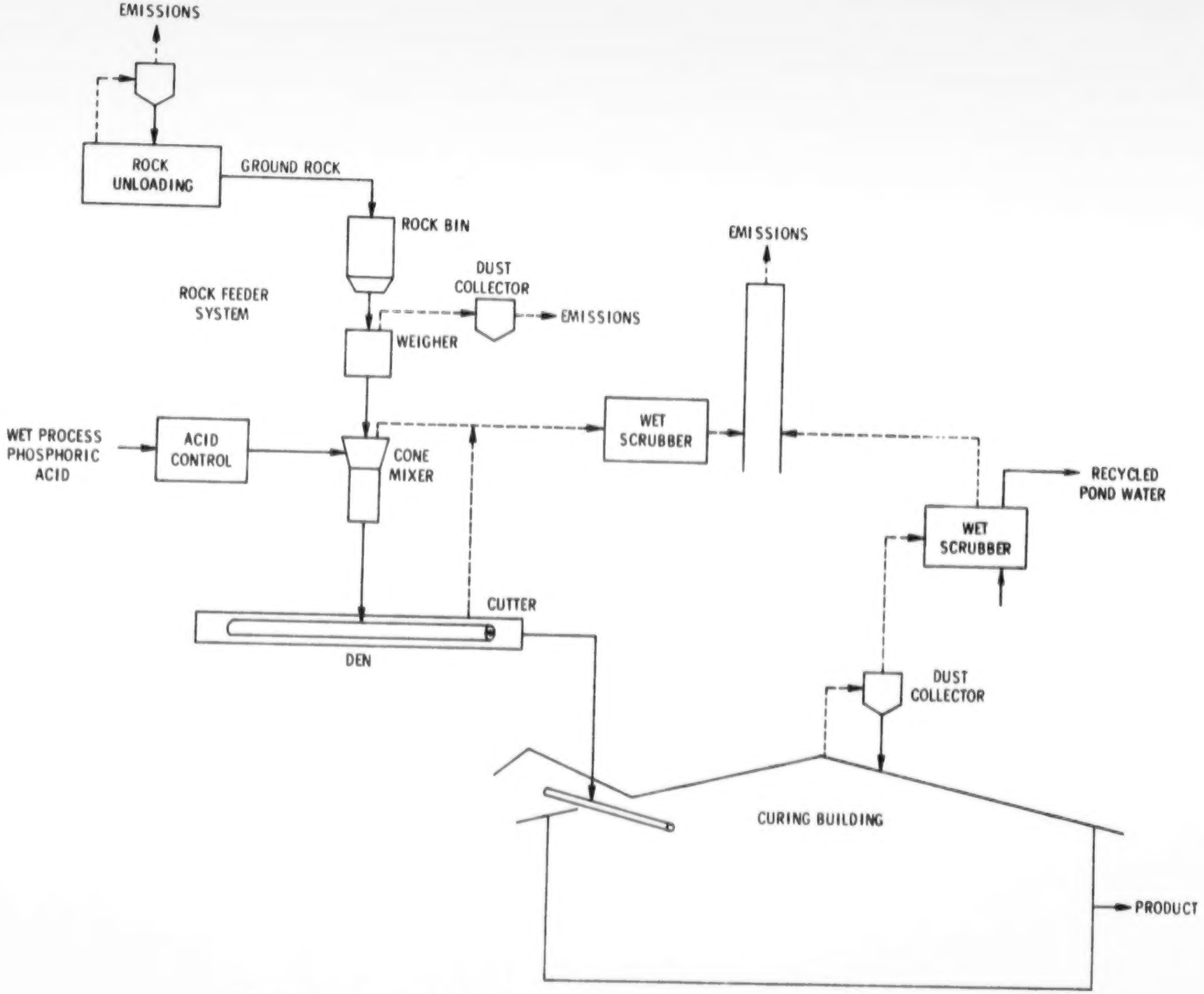
EMISSIONS
ROCK UNLOADING
GROUND ROCK
ROCK BIN
ROCK FEEDER SYSTEM
DUST COLLECTOR
EMISSIONS
WEIGHER
EMISSIONS
WET PROCESS PHOSPHORIC ACID
ACID CONTROL
CONE MIXER
WET SCRUBBER
RECYCLED POND WATER
WET SCRUBBER
CUTTER
DEN
DUST COLLECTOR
CURING BUILDING
PRODUCT

Figure 20. ROP-TSP production facility (31).

at a typical ROP-TSP production facility are similar to those described for an NSP plant. Emissions of fluoride vapors and particulates from the cone mixer, den, and curing building are controlled by wet scrubbers using recirculated pond water. Particulate emissions from ground rock storage and transfer facilities are controlled by baghouse collectors.

b. Granular Triple Superphosphate--
Granulation is employed as a means of improving the storage and handling properties of fertilizer materials. This process yields larger, more uniform particles (mean particle diameters between 1 mm and 4 mm) either by agglomeration of ROP material or by direct granulation of raw product slurry.

(1) GTSP from ROP-TSP--A generalized flow diagram of the process for the production of GTSP from cured ROP-TSP is shown in Figure 21 (4, 16, 31). Less than 10% of the GTSP consumed in the United States is currently produced by this method.

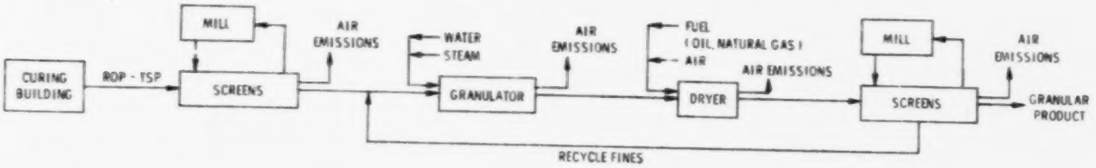

Figure 21. Production of GTSP from cured ROP-TSP (4, 16, 31).

In this process, cured ROP-TSP product is removed from storage and sent to a pulverizer where it is ground and screened. The screened material is then sent to a rotary drum granulator. The addition of steam and water aids the granulation process. The resultant wet granules are discharged to an air dryer where water is evaporated to give a hard, dense, granular product. The discharge from the dryer is screened, and acceptable product is sent to storage. Oversized material is recycled to the pulverizer and undersized to the granulator.

(2) Basic GTSP Process--Two methods for the direct production of GTSP are currently available: 1) Dorr-Oliver slurry granulation process and 2) TVA one-step granulation process. Direct granulation using the Dorr-Oliver process accounts for over 90% of total GTSP production, whereas the one-step process developed by the TVA during the past 10 yr to 15 yr remains experimental (4, 17, 31). The Dorr-Oliver slurry granulation process is illustrated in Figure 22 (16, 31). In this process, phosphate rock, ground to a fineness located between specific particle size levels (80% through a 150-μm screen and 95% through a 75-μm screen), is mixed with phosphoric acid in a reactor or mixing tank. The phosphoric acid used in this process is appreciably lower in concentration (40% P_2O_5) than that used in ROP-TSP manufacture because the

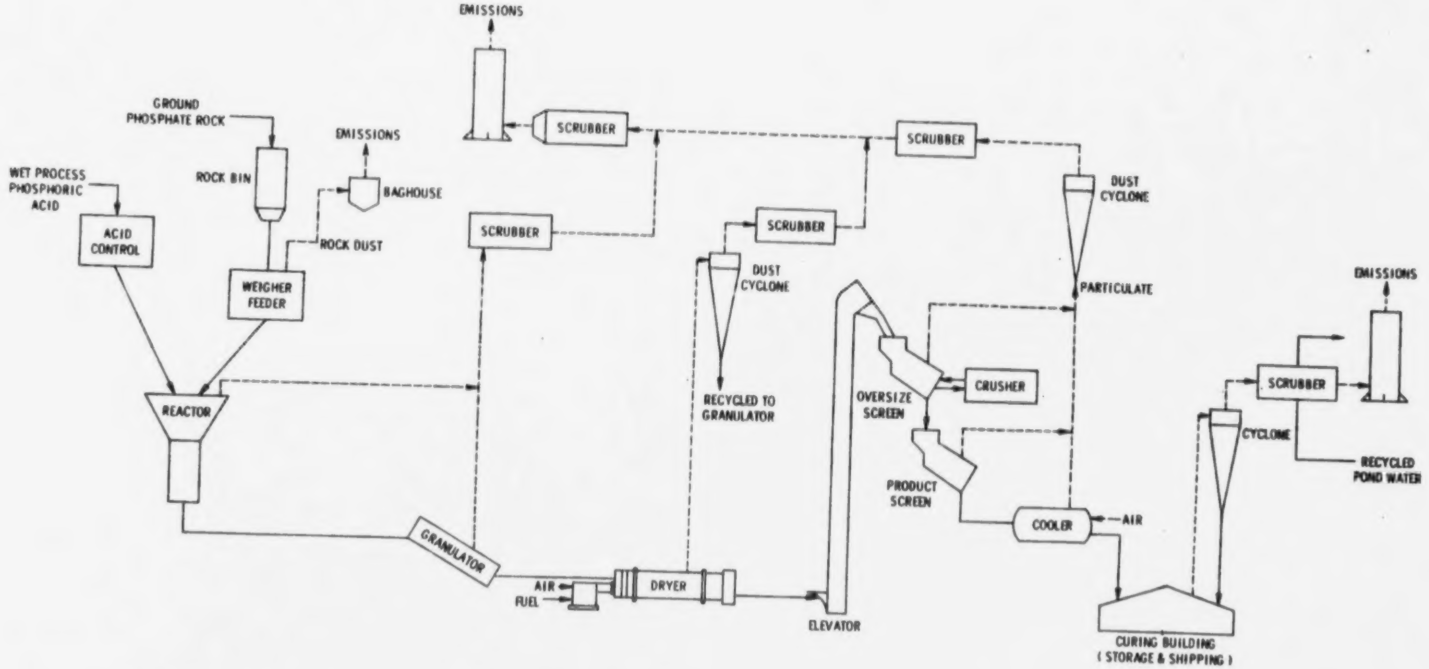
EMISSIONS
GROUND PHOSPHATE ROCK
EMISSIONS
WET PROCESS PHOSPHORIC ACID
ROCK BIN
BAGHOUSE
SCRUBBER
SCRUBBER
ACID CONTROL
SCRUBBER
ROCK DUST
SCRUBBER
DUST CYCLONE
WEIGHER FEEDER
DUST CYCLONE
PARTICULATE
EMISSIONS
CRUSHER
SCRUBBER
REACTOR
RECYCLED TO GRANULATOR
OVERSIZE SCREEN
CYCLONE
RECYCLED POND WATER
PRODUCT SCREEN
COOLER
AIR
GRANULATOR
AIR
FUEL
DRYER
ELEVATOR
CURING BUILDING (STORAGE & SHIPPING)

Figure 22. Dorr-Oliver slurry granulation process for TSP (16, 31).

lower strength acid maintains the slurry in a fluid state during a mixing period of 1 hr to 2 hr (17, 20, 33). A thin slurry is continuously removed and distributed onto dried, recycled fines where it coats out on the granule surfaces and builds up the granule size.

Pugmills and rotating drum granulators are used in the granulation process. A pugmill is composed of a U-shaped trough carrying twin contrarotating shafts upon which are mounted strong blades or paddles. Their action agitates, shears, and kneads the solid-liquid mix, and transports the material along the trough.

The basic rotary drum granulator consists of an open-end, slightly inclined rotary cylinder, with retaining rings at each end and a scraper or cutter mounted inside the drum shell. Drums vary in diameter from 2 m to 3 m and in length from 3 m to 6 m. A rolling bed of dry GTSP material is maintained in the unit while the liquid slurry is introduced through horizontal, multioutlet distributor pipes set lengthwise in the drum under the bed.

Slurry-wetted granules then discharge onto a rotary dryer where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are then sized on vibrating screens. Oversized particles are crushed and recirculated to the screen, while undersized (smaller than 1 mm) particles are recycled to the granulator. Product-sized (1 mm to 4 mm) granules are cooled in a countercurrent rotary drum cooler. The product is then sent to a storage pile for curing. After a curing period of 3 days to 5 days, granules are removed from storage, screened, bagged and shipped (31).

In the TVA one-step granulation process, ground phosphate rock and recycled fines are fed directly into the acidulation drum along with concentrated phosphoric acid and steam. Granulation occurs in this revolving cylindrical reactor. The use of steam accelerates the reaction and ensures an even distribution of moisture in the mix. A more concentrated phosphoric acid (containing 73.5% P_2O_5) can be used, resulting in a higher grade granular product containing about 54% available P_2O_5 (32). After granulation occurs in the reaction cylinder, granules are screened, cooled, and sent to storage in a manner similar to that described for the Dorr-Oliver process.

Emissions of fluorine compounds, SO_x, and dust particles occur during the production of GTSP by the Dorr-Oliver process (16, 31). Silicon tetrafluoride and hydrogen fluoride are released by the acidulation reaction and evolve from the reactor, granulator,

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(33) Final Guideline Document: Control of Fluoride Emissions From Existing Phosphate Fertilizer Plants. EPA-450/2-77-005 (PB 265 062), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977. 277 pp.

dryer, and cooler. Evolution of fluorides continues at a lower rate in the curing building as the reaction proceeds. SO_x enter the dryer exhaust stream as a result of the sulfur composition of the fuel oil. Sources of particulate emissions include the reactor, granulator, dryer, cooler, screens, mills, and transfer conveyors. Additional emissions of particulate result from the unloading, storage, and transfer of ground phosphate rock.

At a typical plant, emissions from the reactor and granulator are controlled by scrubbing the effluent gas with recycled pond water. Emissions from the dryer, cooler, screens, mills, product transfer systems, and storage building are sent to a cyclone separator for removal of a portion of the dust loading before being sent to wet scrubbers (31). Baghouses are used to control the fine rock particulate caused by the preliminary ground rock handling activities.

3. Industry Characterization

For TSP production, two distinct plant types are considered: ROP-TSP and GTSP.

a. Run-of-Pile Triple Superphosphate

An average ROP-TSP plant produces 59,700 metric tons of P_2O_5 per year and is located in a county having a population density of 86.1 persons/km². Average plant production was obtained by dividing the total amount of ROP-TSP produced in 1975 (597,110 metric tons P_2O_5 per year) by the total number of ROP-TSP plants; i.e., 10.

b. Granular Triple Superphosphate

An average GTSP plant is defined as one that produces 69,100 metric tons of P_2O_5 per year by the Dorr-Oliver slurry granulation process and is located in a county having a population density of 73.8 persons/km². The average plant production rate was calculated by dividing the total amount of GTSP produced in 1975 (898,900 metric tons P_2O_5 per year) by the total number of GTSP plants; i.e., 13.

F. AMMONIUM PHOSPHATE PRODUCTION

1. Source Definition

Ammonium phosphates are produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphate fertilizers are produced in the United States. Ammoniated superphosphates are also produced by adding NSP or TSP to the mixture. In this study, only granulation of phosphoric acid with anhydrous ammonia by ammoniation-granulation to produce granular fertilizers will be discussed. An environmental source assessment of the production of liquid ammonium phosphates and ammoniated superphosphates is separately reported in Reference 5.

Approximately 99% of ammonium phosphates are used as fertilizers, with the remaining quantity consumed in fire retardants; as additives to livestock feed; in manufacture of yeast, vinegar, and bread improvers; in flux for soldering; and for sugar purification (34, 35). As fertilizers, product nutrient analyses for typical ammonium phosphates range from 11% to 21% nitrogen and 20% to 55% P_2O_5 (1). Important ammonium phosphate fertilizer grades in the United States are

Primarily monoammonium phosphates (MAP)

11-48-0	11-55-0
13-52-0	16-20-0

Primarily diammonium phosphates (DAP)

16-48-0	18-46-0

where N-P-K analysis represents

N = percentage of available nitrogen
P = percentage of available P_2O_5
K = percentage of soluble potassium oxide (K_2O)

In 1975, 84% (on a P_2O_5 basis) of the ammonium phosphates produced consisted of DAP grade (9). When used as fertilizers, ammonium phosphates are either used directly or blended with other fertilizers, either in liquid or solid form, to produce mixed fertilizers. However, due to the nature of various reporting systems and the complexity of the fertilizer industry, it is impossible to extract amounts of ammonium phosphates used for each application (5).

Emissions from production of mixed fertilizers using granular ammonium phosphates are addressed in "Source Assessment: Fertilizer Mixing Plants" (5). Consequently, this document will discuss emissions from production of granular ammonium phosphates and will encompass process operations from feeding of raw materials to loading of product for shipment.

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(34) David, M. L., J. M. Malk, and C. C. Jones. Economic Analysis of Effluent Guidelines Fertilizer Industry. EPA-230/2-74-010 (PB 241 315), U.S. Environmental Protection Agency, Washington, D.C., January 1974.

(35) The Condensed Chemical Dictionary, Eighth Edition, G. G. Hawley, ed. Van Nostrand Reinhold Company, New York, New York, 1971. p. 54.

2. Process Chemistry

The ternary solubility diagram (ammonia-phosphoric acid-water) presented in Figure 23 (36) identifies four potential anhydrous salts of ammonia and phosphoric acid having NH_3:H_3PO_4 mole ratios of 7:3, 2:1, 1:1, and 1:2. $NH_4H_2PO_4$ (MAP, mole ratio 1:1) and $(NH_4)_2HPO_4$ (DAP, mole ratio 2:1) are salts of commercial fertilizer importance. These desired products are obtained by operating along the solubility boundary at required conditions; i.e., operation along the segment marked DAP yields DAP, while operation along the segment marked MAP yields MAP. Lines from the solubility curve to the right-hand border on Figure 23 represent paths along which solution composition would change during crystallization or solution (36).

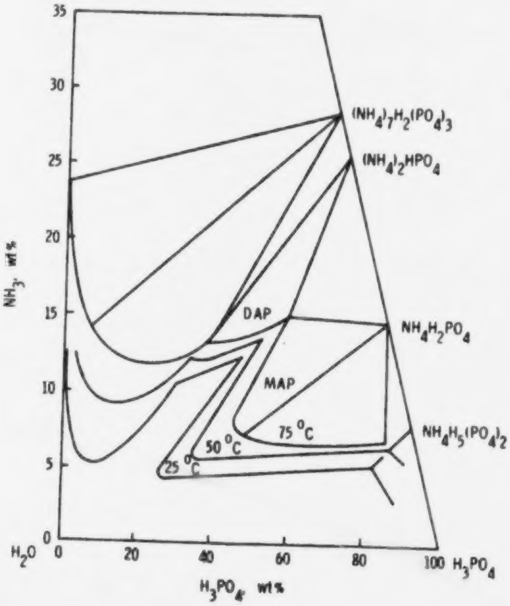

Figure 23. Solubility boundaries for the ammonia-phosphoric acid-water system (36).

Reprinted from The Chemistry and Technology of Fertilizers by courtesy of the American Chemical Society.

Production of commercial ammonium phosphates is based on four exothermic reactions. MAP is produced from 1 mole of phosphoric acid and 1 mole of ammonia, yielding a product having 12.2%

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(36) Chemistry and Technology of Fertilizers. V. Sauchelli, ed. Reinhold Publishing Corp., New York, New York, 1960. pp. 251-268.

nitrogen (N) and 61.7% available phosphorus (P_2O_5); i.e., 12-62-0, while releasing 105 kJ/mole (37, 38).

$$H_3PO_4 + NH_3 \longrightarrow NH_4H_2PO_4 \qquad (12)$$

DAP production combines 1 mole of phosphoric acid with 2 moles of ammonia yielding a product having 21.2% nitrogen and 53.8% available phosphorus; i.e., 21-54-0, while releasing 159 kJ/mole (37, 38).

$$H_3PO_4 + 2NH_3 \longrightarrow (NH_4)_2HPO_4 \qquad (13)$$

MAP also reacts with ammonia to produce DAP and 54 kJ/mole (37, 38).

$$NH_4H_2PO_4 + NH_3 \longrightarrow (NH_4)_2HPO_4 \qquad (14)$$

To attain various desired product analyses, sulfuric acid is added in appropriate quantities and reacts with ammonia to form ammonium sulfate and to release 138 kJ/mole (17, 37, 38).

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4 \qquad (15)$$

Properties of pure crystalline MAP and DAP are listed in Table 15 (36, 37, 39) and presented in Figure 24.

Analyses of raw materials for ammonium phosphate manufacture are presented in Table 16. Ammonium phosphates can be made from either furnace process phosphoric acid or WPPA. Impurities in WPPA prevent production of fertilizers having analyses equivalent to pure MAP or DAP composition. For some products, e.g., 16-20-0, diluents such as sulfuric acid are added to phosphoric acid by design to reduce available phosphorus content of product to desired levels. Commercial grades of ammonium phosphate range from MAP grade 11-48-0 to DAP grade 18-46-0. Intermediate grades identified earlier are either mixtures of MAP and DAP or diluted MAP or DAP.

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(37) Waggaman, W. H. Phosphoric Acid, Phosphates, and Phosphatic Fertilizers, Second Edition. Reinhold Publishing Corp., New York, New York, 1952. pp. 308-344.

(38) Himmelblau, D. M. Basic Principles and Calculations in Chemical Engineering, Second Edition. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1967. pp. 449-454.

(39) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 9. John Wiley & Sons, Inc., New York, New York, 1966. pp. 46-132.

TABLE 15. PROPERTIES OF PURE AMMONIUM PHOSPHATES (36, 37, 39)

Property	MAP	DAP
N, %	12.2	21.2
P_2O_5, % available	61.7	53.8
Heat of formation, kJ/mole	-1,450.8	-1,573.7
Specific gravity at 19°C	1.803	1.619
Solubility, g/100 g H_2O:		
At 20°C	37.4	69.0
At 40°C	56.7	81.0
At 75°C	108.8	108.7
Dissociation pressure, Pa:		
At 100°C	Negligible	670
At 125°C	6.7	4,000

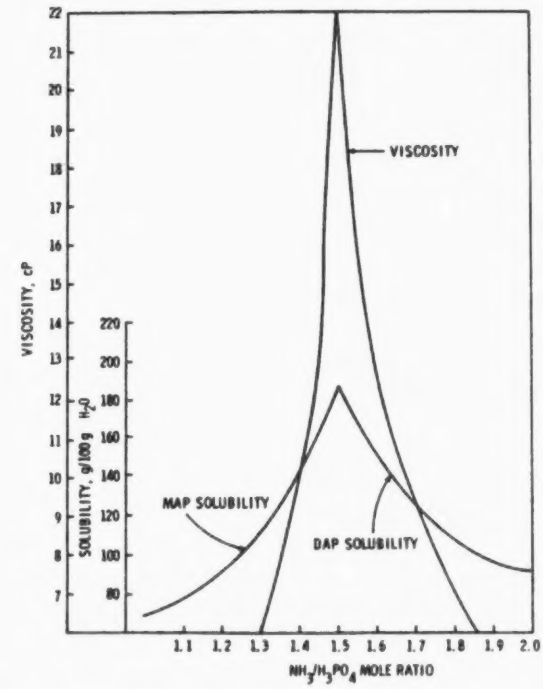

Figure 24. Ammonium phosphate solubility and viscosity as a function of $NH_3:H_3PO_4$ mole ratio (36).

Reprinted from The Chemistry and Technology of Fertilizers by courtesy of the American Chemical Society.

TABLE 16. COMPOSITION OF AMMONIUM PHOSPHATE RAW MATERIALS (22, 37, 40, 41)

Component	Composition, wt %			Furnace process phosphoric acid,[a] ppm
	Anhydrous ammonia	WPPA (average)		
		Filtered	Concentrated	
NH_3	99.9	–[b]		
P_2O_5		28.7	53.3	54.32 wt %
Ca		0.30	0.06	0.0
Fe		0.45	0.78	2
Al		0.29	0.52	0.0
Mg		0.13	0.26	
Cr			0.02	0.2
V			0.02	
Na		0.05	0.45	0.01 wt %
K		0.02	0.06	0.0
F		1.82	0.56	0.4
SO_3		2.11	2.3	0.0
SiO_2		0.79	0.16	0.0
C			0.24	
Solids			3.7	
Cl				
Pb				2
Cu				0.2
As				0.1

[a] Commercial food-grade phosphoric acid.

[b] Blanks indicate data not applicable.

3. Process Description

Two basic mixer designs are used by ammoniation-granulation plants: pugmill ammoniator and rotary-drum ammoniator. Approximately 95% of ammoniation-granulation plants in the United States use a rotary-drum mixer developed and patented by the TVA (5). The primary product of this technology is 18-46-0, consisting primarily of DAP. Ammonium phosphate products having a lower $NH_3:H_3PO_4$ mole ratio are made using the Dorr-Oliver process or variations of it. The degree of ammoniation utilized with this technology ranges from an $NH_3:H_3PO_4$ mole ratio of 1.0 to 1.8, and the primary product is 16-48-0, a product containing approximately one-third MAP and two-thirds DAP.

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(40) Slack, A. V. Fertilizer Developments and Trends. Noyes Development Corp., Park Ridge, New Jersey, 1968. pp. 77-274.

(41) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 15. John Wiley & Sons, Inc., New York, New York, 1968. p. 260.

a. TVA Process--

A general process flow diagram of the TVA ammonium phosphate process is presented in Figure 25. Phosphoric acid is mixed in an acid surge tank with 93% sulfuric acid (used for product analysis control) along with recycle and acid from wet scrubbers. Mixed acids have a P_2O_5 content of 40% to 45% (42). This analysis is attained by mixing unconcentrated filtered WPPA, 28.7% P_2O_5, and concentrated WPPA, 53.3% P_2O_5 (see Table 16) (11, 40).

Mixed acids are then partially neutralized with liquid or gaseous anhydrous ammonia in an brick-lined acid reactor. In this agitated atmospheric pressure tank, the mole ratio of $NH_3:H_3PO_4$ is maintained at 1.3:1.0 to 1.5:1.0 (16, 39, 42-44). All phosphoric acid and approximately 70% of ammonia are introduced in this vessel (45). In this molar range, ammonium phosphates are most soluble, allowing further concentration of solution while maintaining adequate flow characteristics (Figure 24). Heat of reaction is used in this vessel to maintain a temperature of 100°C to 120°C and to evaporate excess water (39, 43). A slurry which is primarily MAP and contains 18% to 22% water is produced and flows through steam-traced lines to the ammoniator-granulator (43). To assure no leakage from the reactor, the vessel is ventilated with outside air. In theory, the reactor could be designed without ventilation or atmospheric discharge, but in practice, ventilation rates of 57 to 71 m^3/min (standard conditions) are common. Ventilation rate is determined by reactor mechanical design, not process requirements (45). Ammonia-rich offgases from the reactor at 77°C to 82°C are wet scrubbed before exhausting to the atmosphere (45). Primary scrubbers use raw material-mixed acids as scrubbing liquor, and secondary scrubbers use gypsum pond water as scrubbing liquor.

The basic rotary-drum ammoniator-granulator, Figure 26, consists of an open-end, slightly inclined rotary cylinder with retaining rings at each end and a scraper or cutter mounted inside the drum

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(42) Shreve, R. N. Chemical Process Industries, Third Edition. McGraw-Hill Book Company, New York, New York, 1967. pp. 274-277.

(43) Chopey, N. P. Diammonium Phosphate: New Plant Ushers in Process Refinements. Chemical Engineering, 69(6):148-150, 1962.

(44) Vandegrift, A. E., L. J. Shannon, E. W. Lawless, P. G. Gorman, E. E. Sallee, and M. Reichel. Particulate Pollutant System Study, Vol. 3--Handbook of Emission Properties. APTD-0745 (PB 203 522), U.S. Environmental Protection Agency, Durham, North Carolina, 1971. pp. 313-335.

(45) Hardison, L. C. Air Pollution Control Technology and Costs in Seven Selected Areas. EPA-450/3-73-010 (PB 231 757), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1973. pp. 11-192.

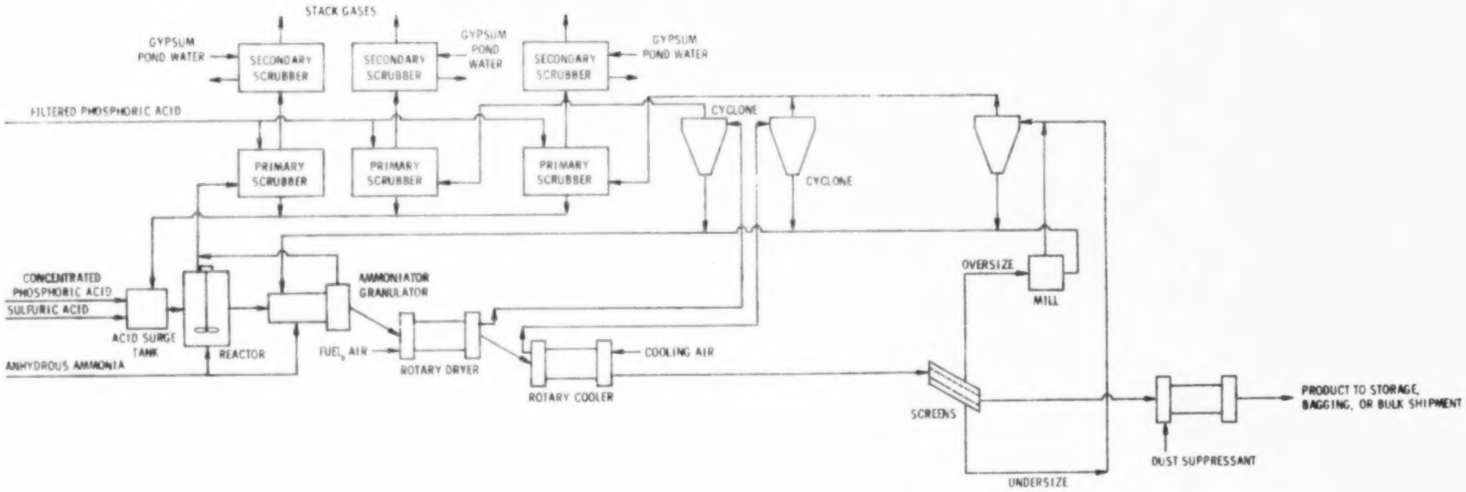
STACK GASES
GYPSUM POND WATER
SECONDARY SCRUBBER
SECONDARY SCRUBBER
GYPSUM POND WATER
SECONDARY SCRUBBER
GYPSUM POND WATER
FILTERED PHOSPHORIC ACID
CYCLONE
PRIMARY SCRUBBER
PRIMARY SCRUBBER
PRIMARY SCRUBBER
CYCLONE
CONCENTRATED PHOSPHORIC ACID
SULFURIC ACID
ACID SURGE TANK
REACTOR
AMMONIATOR GRANULATOR
ANHYDROUS AMMONIA
FUEL, AIR
ROTARY DRYER
ROTARY COOLER
COOLING AIR
OVERSIZE
MILL
SCREENS
UNDERSIZE
DUST SUPPRESSANT
PRODUCT TO STORAGE, BAGGING, OR BULK SHIPMENT

Figure 25. TVA ammonium phosphate process flow diagram.

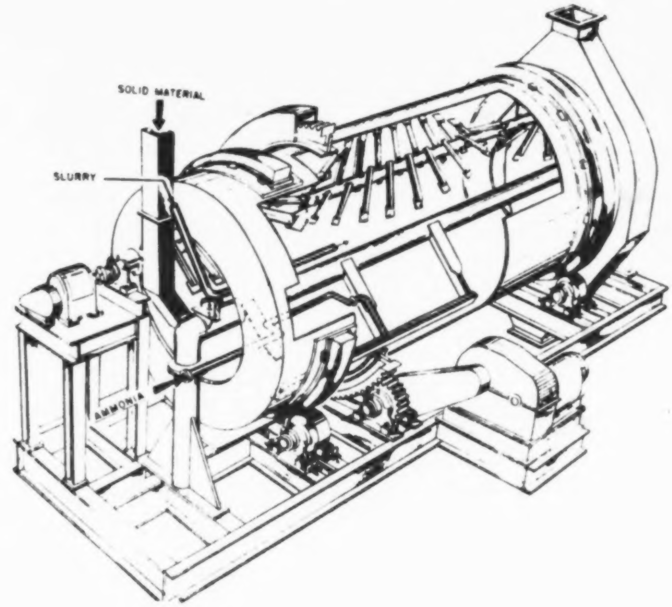

Figure 26. TVA rotary ammoniator-granulator (5).

shell. Drums vary in diameter from 2 m to 3 m and in length from 3 m to 6 m. A rolling bed of recycled solids is maintained in the unit; slurry from the reactor is distributed above the bed while the remaining ammonia (approximately 30%) is sparged underneath to bring the final NH_3:H_3PO_4 mole ratio from 1.8:1.0 to 2.0:1.0 (5, 45). Granulation by agglomeration and by coating particles with slurry takes place in the rotating drum and is completed in the dryer. Recycle rates of 2.5 to 4.0 kg recycle/kg product are typical for this type of unit (39). As with the reactor, the granulator theoretically could be designed without ventilation, but to prevent NH_3 leakage, approximately 8.5×10^{-4} m^3 (standard conditions) per metric ton P_2O_5 air inleakage into the granulator around inlet and outlet connections is allowed (45).

Temperature of granular DAP in the rotary drum reaches 85°C to 105°C, while temperature of offgases reaches 38°C to 77°C (5, 43, 45). Ammonia-rich offgases pass through a wet scrubber before exhausting to the atmosphere.

Moist DAP granules are transferred to a rotary oil- or gas-fired cocurrent dryer which reduces product moisture content to below 2%, and then product is cooled to below 35°C. Cooling minimizes caking and product dissociation during storage (see Table 15)

(43, 46). Temperature of offgases from the dryer ranges from 82°C to 104°C, and temperature of offgases from the cooler ranges from 4°C to 27°C (5, 45). Before exhausting to the atmosphere, these offgases pass through cyclones and wet scrubbers.

Cooled granules pass to a double-deck screen in which oversize and undersize particles are separated from product-sized particles (42, 47). Some plants screen the product before cooling (42, 44). DAP product ranges in granule size from 1 mm to 4 mm, with a typical product size distribution presented in Figure 27 (5, 48). The oversize are crushed, mixed with the undersize, and recycled to the ammoniator-granulator. To reduce DAP dustiness, some manufacturers coat product granules with 0.5% by weight of 10-wt lubricating oil using a rotating dust suppressant system similar to that shown in Figure 28 (46, 49). DAP is either stored, bagged, or bulk loaded for shipment.

b. Dorr-Oliver Process--

A general process flow diagram of the Dorr-Oliver process is presented in Figure 29. Phosphoric acid (24% to 36% P_2O_5) (37) or a mixture with sulfuric acid is fed to a series of agitated reactors in which acids react with liquid or gaseous anhydrous ammonia feed. The bulk of the reaction takes place in the first reactor, with additional vessels used for pH adjustment of resulting slurry (37). Reactor offgases are scrubbed with raw phosphoric acid feed prior to exhausting to the atmosphere (17).

Thick slurry from the final reactor flows to a pugmill (blunger) where recycled fines are added and product is granulated (39, 40). A blunger, Figure 30, is an inclined vessel with parallel contrarotating shafts having blades to facilitate slurry mixing and progress through the vessel. Recycle ratios range from 6 to 12 kg recycle/kg product (37, 39). These ratios are higher than those for processes having further ammoniation during granulation for two reacons: 1) less water is evaporated in the blunger

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(46) Achorn, F. P., and H. L. Balay. Systems for Controlling Dust in Fertilizer Plants. In: TVA Fertilizer Conference, Tennessee Valley Authority Bulletin Y-78, Muscle Shoals, Alabama, August 1974. pp. 55-62.

(47) Phosphate Fertilizer Plants Final Guideline Document Availability. Federal Register, 42(40):12022-12023, 1977.

(48) Hoffmeister, G. Quality Control in a Bulk Blending Plant. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 59-70.

(49) Barber, J. C. Environmental Control in Bulk Blanding Plants. 1. Control of Air Emissions. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 39-46.

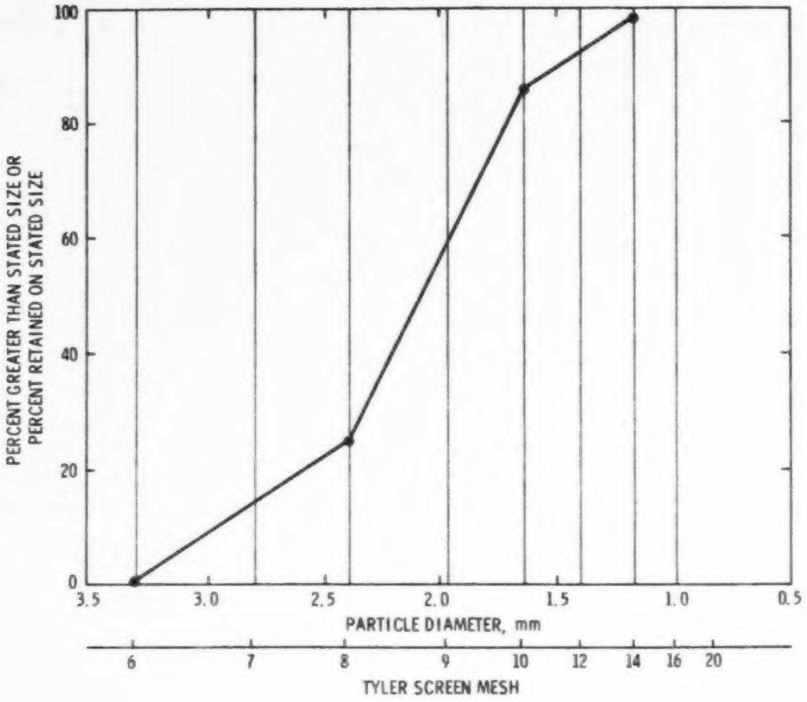

Figure 27. Cumulative screen analysis of DAP (43).

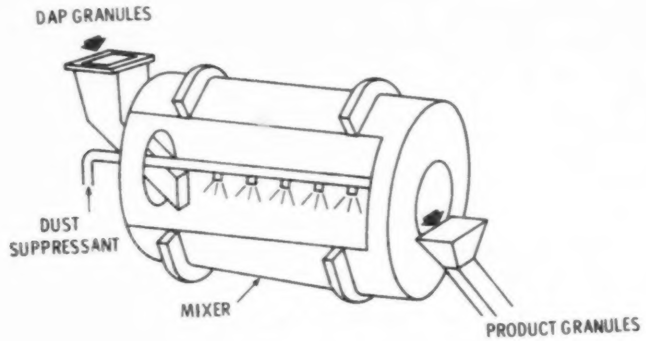
DAP GRANULES
DUST SUPPRESSANT
MIXER
PRODUCT GRANULES

Figure 28. Product dust control system (49).

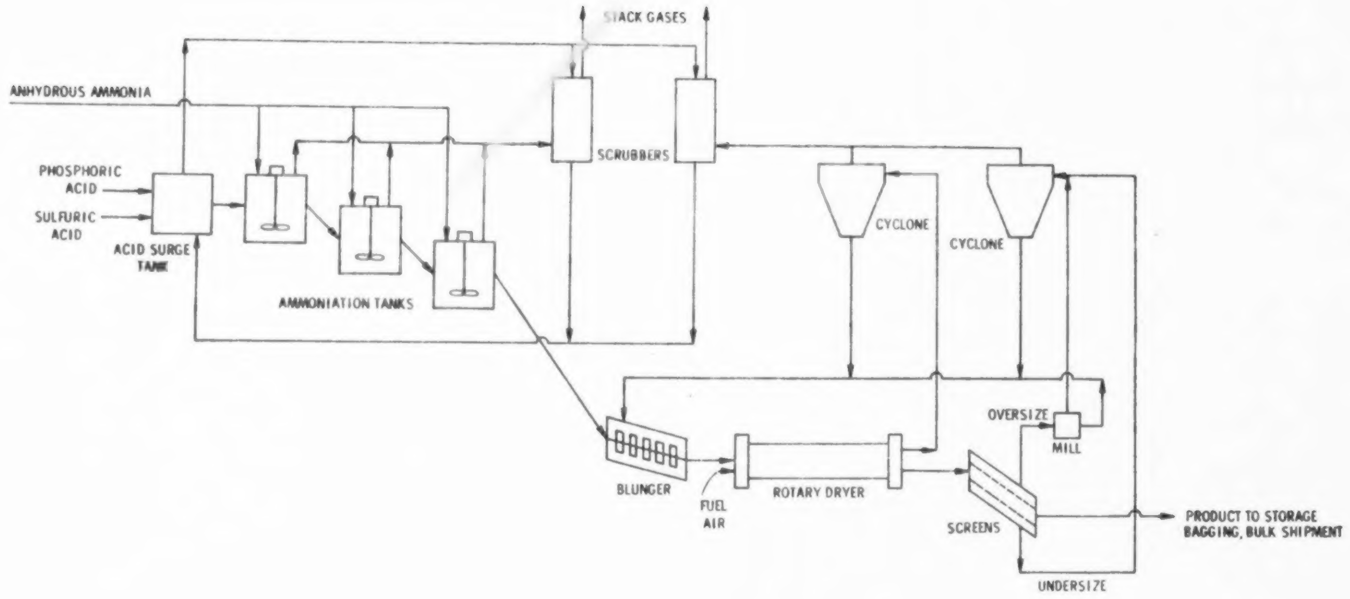
STACK GASES
ANHYDROUS AMMONIA
SCRUBBERS
PHOSPHORIC ACID
SULFURIC ACID
ACID SURGE TANK
AMMONIATION TANKS
CYCLONE
CYCLONE
OVERSIZE
MILL
BLUNGER
FUEL
AIR
ROTARY DRYER
SCREENS
PRODUCT TO STORAGE BAGGING, BULK SHIPMENT
UNDERSIZE

Figure 29. Dorr-Oliver ammonium phosphate process flow diagram.

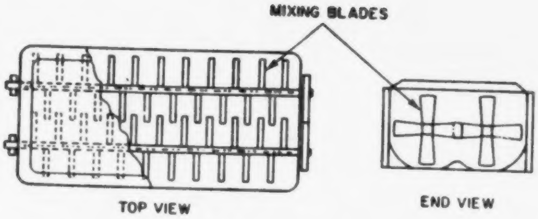

Figure 30. Diagram of pugmill (blunger); top and end views (1).

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during granulation and 2) at a lower $NH_3:H_3PO_4$ mole ratio, product slurry has higher solubility (see Figure 24) (39).

Slurry-coated granules are then dryed in a cocurrent rotary dryer. Product is then sized, e.g., 2.4 mm to 1.7 mm granules, and oversize are crushed, mixed with undersize, and recycled to the blunger (36). Product is sent to bulk storage for bagging or bulk shipment. Offgases are vented to the atmosphere through a cyclone and wet scrubber (16).

4. Industry Characterization

Recent production history of the ammonium phosphate fertilizer industry is presented in Figure 31. Reported production data are for MAP and DAP materials and their processed combinations with ammonium sulfate. Ammonium phosphates produced in combination with potash salts to make complete mixtures are excluded. Also excluded are nitrophosphates, calcium metaphosphates, sodium phosphates, and wet-base goods (made by treating phosphate rock and some organic nitrogenous materials with sulfuric acid) (9).

All production and capacity data in this report are presented as metric tons of P_2O_5. The relationship between metric tons of P_2O_5 and metric tons of gross fertilizer product is a function of fertilizer nutrient analysis and is therefore variable from plant to plant and within each plant as a function of time. A general conversion factor for the entire industry in 1975 was (see Appendix A) (50-61).

$$\text{Gross fertilizer (metric tons)} = 2.49[P_2O_5 \text{ (metric tons)}] \qquad (16)$$

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(49) Inorganic Fertilizer Materials and Related Products. M28B(75)-11, U.S. Department of Commerce, Washington, D.C., January 1976. 6 pp.

(50) Inorganic Fertilizer Materials and Related Products. M28B(75)-12, U.S. Department of Commerce, Washington, D.C., February 1976. 6 pp.

(continued)

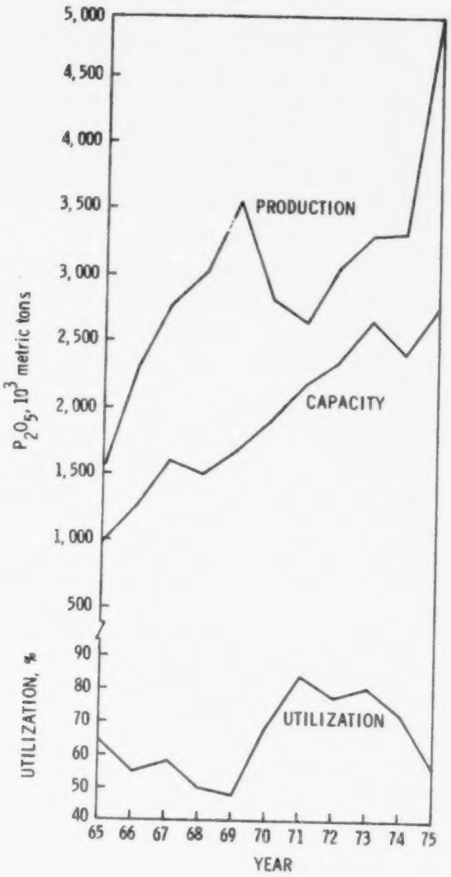

Figure 31. Recent history of ammonium phosphate capacity and production (7, 9-11, 34).

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(52) Inorganic Fertilizer Materials and Related Products. M28B(76)-1, U.S. Department of Commerce, Washington, D.C., March 1976. 6 pp.

(53) Inorganic Fertilizer Materials and Related Products. M28(76)-2, U.S. Department of Commerce, Washington, D.C., April 1976. 6 pp.

(54) Inorganic Fertilizer Materials and Related Products. M28(76)-3, U.S. Department of Commerce, Washington, D.C., May 1976. 6 pp.

(55) Inorganic Fertilizer Materials and Related Products. M28(76)-4, U.S. Department of Commerce, Washington, D.C., June 1976. 6 pp.

(56) Inorganic Fertilizer Materials and Related Products. M28(76)-5, U.S. Department of Commerce, Washington, D.C.,

(continued)

From 1965 to 1975, ammonium phosphate production grew from 0.983 x 10^6 metric tons P_2O_5 to 2.767 x 10^6 metric tons P_2O_5 (an annual growth rate of approximately 11%), while capacity grew from 1.512 x 10^6 metric tons P_2O_5 to 4.926 x 10^6 metric tons P_2O_5 (an annual growth rate of approximately 12%). Over that period, plant utilization rates varied from 47% to 83%, ending in 1975 at 56%. For the period 1970 to 1975, the average annual utilization rate was 73%.

In 1975, 35 companies in the United States operated 48 ammonium phosphate plants in 17 states (see Appendix A). Distribution of plants and capacity by state in Table 17 (7, 10, 11) indicates that Florida is the largest ammonium phosphate-producing state (25% of plants nationally having 43% of national capacity). Florida and Louisiana, with 35% of ammonium phosphate plants, have 67% of national capacity. As shown in Table 18, 8 of the 35 companies have an annual capacity of over 200,000 metric tons P_2O_5; combined, they represent 64% of total national capacity.

A cumulative distribution of ammonium phosphate plants and capacity in 1975 is presented in Figure 32. The distribution shows that many small plants collectively represent a small fraction of capacity while a few large plants represent a large fraction of capacity. From the graph, 50% of the plants each have annual capacity of less than approximately 65,000 metric tons P_2O_5, but these plants represent only approximately 15% of total national capacity. Conversely, 50% of national capacity is represented by plants each having annual capacity of less than approximately 180,000 metric tons P_2O_5. Approximately 83% of plants are below this size. Mean plant capacity in 1975 was 103,000 metric tons P_2O_5.

(continued)

July 1976. 6 pp.

(57) Inorganic Fertilizer Materials and Related Products. M28(76)-6, U.S. Department of Commerce, Washington, D.C., August 1976. 6 pp.

(58) Inorganic Fertilizer Materials and Related Products. M28(76)-7, U.S. Department of Commerce, Washington, D.C., September 1976. 6 pp.

(59) Inorganic Fertilizer Materials and Related Products. M28(76)-8, U.S. Department of Commerce, Washington, D.C., October 1976. 6 pp.

(60) Inorganic Fertilizer Materials and Related Products. M28(76)-9, U.S. Department of Commerce, Washington, D.C., November 1976. 6 pp.

(61) Inorganic Fertilizer Materials and Related Products. M28(76)-10, U.S. Department of Commerce, Washington, D.C., December 1976.

TABLE 17. 1975 DISTRIBUTION OF AMMONIUM PHOSPHATE CAPACITY BY STATE (7, 10, 11)

State	Capacity, 10^3 metric tons P_2O_5	Percent of national capacity	Number of plants
Florida	2,101	43	12
Louisiana	1,173	24	5
Texas	293	6	4
Idaho	262	5	4
Iowa	228	5	2
Mississippi	139	3	1
California	118	2	7
Illinois	114	2	1
North Carolina	92	2	1
Alabama	86	2	2
Missouri	84	2	1
Utah	65	1	2
Minnesota	63	1	1
Arkansas	45	1	1
Washington	27	<1	1
Michigan	25	<1	2
Arizona	11	<1	1
Total	4,926	100	48

TABLE 18. COMPANIES HAVING AMMONIUM PHOSPHATE CAPACITY $\geq$200,000 METRIC TONS P_2O_5 IN 1975 (7, 10, 11)

Company	Capacity, 10^3 metric tons P_2O_5	Percent of national capacity
CF Industries, Inc.	827	17
Williams Companies, Agrico Chemical Co., Subsidiary	729	15
Beker Industries	328	7
Occidental Petroleum Corp., Occidental Chemical Co., Subsidiary	300	6
Gardinier Inc.	272	6
Farmland Industries, Inc.	248	5
IMC Chemicals Corp.	227	5
Olin Corp.	209	4

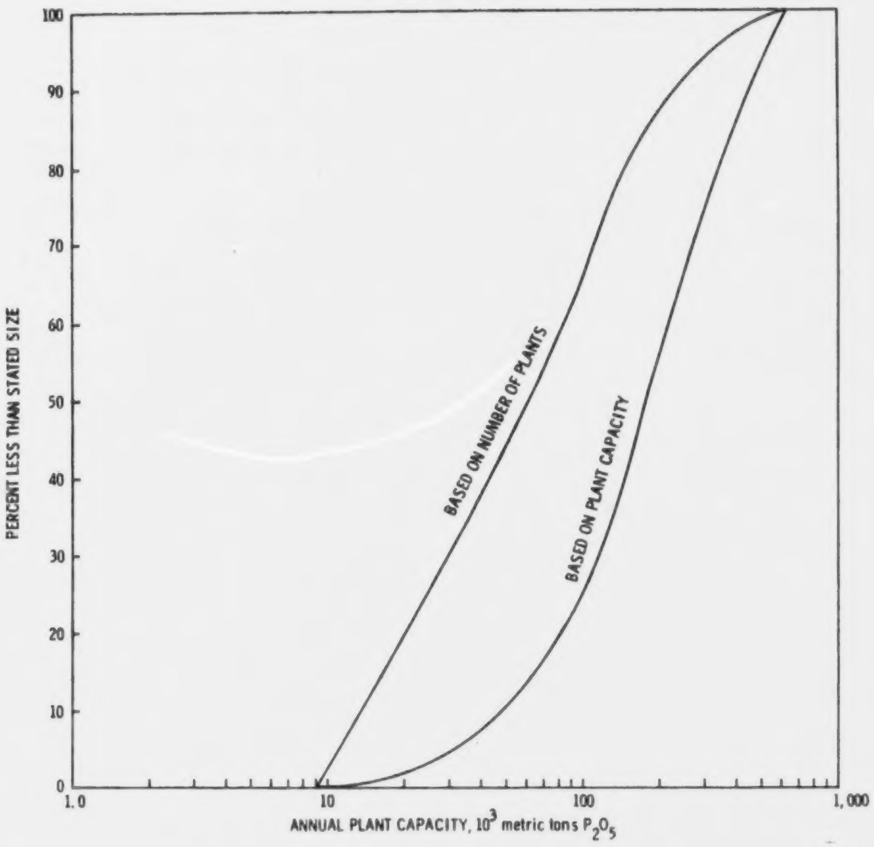

Figure 32. Cumulative distribution of ammonium phosphate plants and capacity in 1975 (7, 10, 11).

As previously mentioned, DAP production using TVA technology with WPPA is representative of the ammonium phosphate industry. An average DAP plant is similar to the one illustrated in Figure 25 and has average parameters. The average plant has a capacity of 103,000 metric tons/yr P_2O_5 and an average annual utilization factor of 73%, yielding an annual production rate of 75,000 metric tons P_2O_5 (Appendix A).

Ammonium phosphate production facilities are located in counties with population densities ranging from 1 person/km² to 1686 persons/km² (Appendix A).

The average plant is located in a county with a population density of 82 persons/km² based on a plant capacity weighted average.

SECTION 4

AIR EMISSIONS

A. WET PROCESS PHOSPHORIC ACID

Production of WPPA generates a variety of gaseous and particulate emission species. These emissions arise from five unit operations in the production process: rock unloading, rock storage and conveying, acidulation, filtration, and evaporation. These unit operations, however, release emissions to the atmosphere in only three locations, as shown in Figure 33: rock unloading, rock storage and conveying, and wet scrubber system. In this study, phosphoric acid production was defined to begin with the unloading of ground rock; however, most large plants in Florida grind their rock on site.

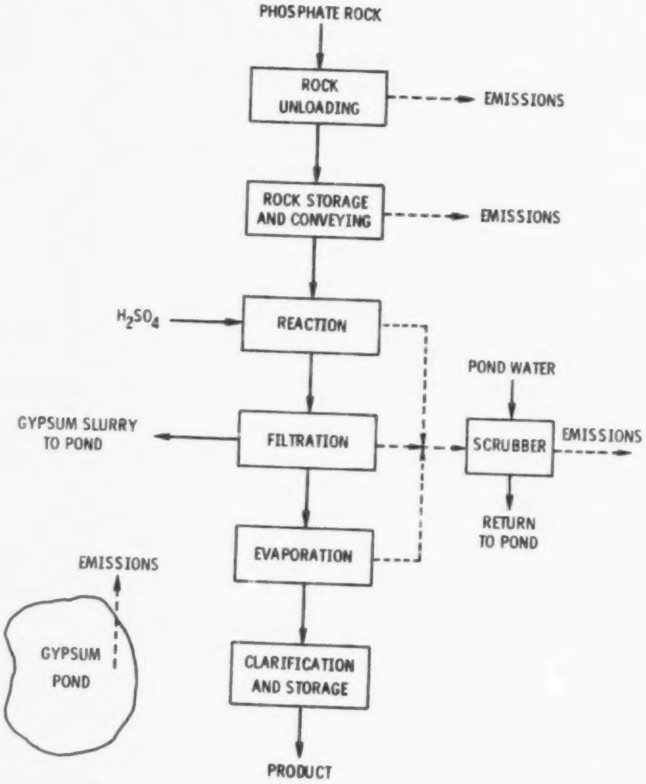
PHOSPHATE ROCK
ROCK UNLOADING
EMISSIONS
ROCK STORAGE AND CONVEYING
EMISSIONS
H_2SO_4
REACTION
POND WATER
GYPSUM SLURRY TO POND
FILTRATION
SCRUBBER
EMISSIONS
RETURN TO POND
EVAPORATION
EMISSIONS
GYPSUM POND
CLARIFICATION AND STORAGE
PRODUCT

Figure 33. Schematic of emission points in WPPA manufacture.

Another source of air emissions at phosphate fertilizer plants is the gypsum pond. Water-soluble fluoride compounds are separated from phosphate rock in the reactor, and a portion is carried to the gypsum pond along with calcium sulfate from the filtration operation. Volatile fluorine compounds evolve from the pond at variable rates depending on gypsum pond characteristics.

1. Raw Materials Handling

Ground phosphate rock transported to the plant by railroad hopper cars or hopper trucks is delivered to rock storage bins and elevated feed bins by combination screw conveyors, bucket elevators, belt conveyors, and pneumatic conveyors. Elevated feed bins allow use of gravity flow to batch weigh hoppers. A small fixed hopper and oversized screw conveyor convert the batch weighings to a uniform feed to the reactor. To properly control rock dust emissions, conveyors, feeders, hoppers, and storage bins are enclosed and vented to dust abatement equipment, typically a baghouse. The unloading shed is also enclosed and equipped with a bag collector for rock recovery and particulate emissions control.

Phosphate rock is ground to 60% to 80% less than 74 μm (minus 200 mesh) for WPPA manufacture. Because no reaction has taken place, the particulate composition is that of the raw material, phosphate rock (17, 22).

Limited data exist on emissions from baghouses associated with rock handling at production facilities. However, some data concerning these emissions, available in public files from the Florida Department of Environmental Regulations, are tabulated in Appendix B.

The controlled particulate emission factor for rock unloading is 0.15 g/kg P_2O_5 ± 250% based on averaging data in Appendix B. Uncertainty associated with the emission factor is calculated using the "Student t" test at a 95% confidence level.

For rock transfer and charging to the reactor, the controlled emission factor ranges from 0.012 to 0.10 g/kg P_2O_5 with an average value of 0.045 g/kg P_2O_5 ± 180% (see Appendix B for data).

The average value and standard deviation for the height of rock unloading emissions is 12 ± 3 m. For rock transfer, the average value is 21 ± 6 m (Appendix B). These values do not necessarily represent stack heights, but an elevated point in the plant where particulates are exhausted. These values will hereafter be referred to as stack heights.

2. Wet Scrubber System

Three operations responsible for creating emission species are discussed concurrently in this section: phosphate rock acidulation, filtration and evaporation. To comply with strict criteria governing emissions, particularly of fluoride compounds, all phosphoric acid plants employ various types of wet scrubbers as control devices. Plants for which emissions data were available have these three unit operations housed under one roof, with one wet scrubber collecting emissions from the operations. For this reason, one controlled emission factor for each emission species is obtained for the multiunit process, based on an average vent height for the wet scrubber system of 29 m (Appendix B). The sources and species of emissions are described below.

a. Fluoride--

Gaseous fluoride emissions consist of silicon tetrafluoride generated in the reaction and evaporation processes. Hydrogen fluoride formed in the reactor is converted to SiF_4 according to the reaction (45):

$$4HF + SiO_2 \longrightarrow 2H_2O + SiF_4 \qquad (17)$$

The reaction favors the formation of SIF_4 at temperatures lower than 100°C.

Phosphate rock typically contains 3.0% to 4.0% (by weight) fluorine which is variably distributed in the product acid, gypsum slurry, and gaseous emissions (20). Table 19 shows two material balances depicting final distributions of the fluorine from the rock. To reduce air emissions, the plants utilize wet scrubbers. Silicon tetrafluoride is removed through reaction with water to form aqueous fluosilicic acid, and hydrogen fluoride is removed from the gaseous stream in the form of aqueous hydrofluoric acid and silicon tetrafluoride.

In 14 plants that represent approximately 50% of total phosphoric acid production, fluorine is recovered in the form of fluosilicic acid, fluorides, fluosilicates, or byproducts (7). The other 22 plants regard the fluorine materials as waste and pump the fluorine-laden scrubbing water with the gypsum slurry to the settling pond. Consequently, emission factors for total fluorine from the scrubber's gaseous exhaust stream were divided into two groups based on whether or not fluorine recovery was practiced (Appendix B). Comparison of the two sets of data indicate that the emission factors are not significantly different. For example, two plants without fluorine recovery have emissions of 0.0033 and 0.0042 g/kg P_2O_5, which compares with two plants with recovery of fluorine which have emission factors of 0.0033 and 0.0055 g/kg P_2O_5. One plant recovering fluorine has an emission factor of 0.011 g/kg P_2O_5 which compares with three plants not recovering fluorine with emission factors of 0.012 g/kg P_2O_5 and

TABLE 19. FLUORINE MATERIAL BALANCES FOR WPPA MANUFACTURE

	Fluorine, 10^6 g/day					
Material balance	Phosphate rock	Product acid	Gypsum slurry and process H_2O	Air emission	Plant daily production, metric tons P_2O_5	Fluorine emission factor, g/kg P_2O_5
A[a]	48.3	36.5	11.8	0.004	368	0.011
B[b]	127	16.3	110.7	0.009	907	0.010

[a] Data obtained from the public files at the Florida Department of Environmental Regulations in Winter Haven, October 1976.

[b] Data from Reference 62.

one with 0.011 g/kg P_2O_5. One plant not recovering fluorine has a reported emission factor of 0.035, which is high. However, this is a very small plant with a capacity of only 6 metric tons per hour P_2O_5 and is no doubt an old plant with a less efficient scrubber. Emission factors probably depend more on the type and efficiency of scrubber used, scrubber operation, and the use of fresh water tail gas scrubbers than on whether fluorine recovery is practiced. Plants practicing fluorine recovery send less volatile fluorine to their pond systems and might have lower total fluorine emissions from their ponds.

An average emission factor for the wet scrubber system was calculated by averaging data from nine plants with 15 trains (Appendix B) with emission factors from the two material balances shown in Table 19. Controlled emission factors at individual plants range from 0.0025 to 0.035 g/kg P_2O_5. The average fluorine emission factor for the wet scrubber system, calculated by averaging all industry data, is 0.01 g/kg P_2O_5 ± 40%.

b. Particulate--

Particulate emissions generated in the reactor consist of unreacted phosphate rock, with lesser amounts of insoluble phosphate salts and calcium sulfate. This dust is physically entrained in reactor gases vented to the scrubber. Lack of data precludes estimating the relative amounts of species in particulate emissions. Some particulate matter contains silica (SiO_2) which is formed when silicon tetrafluoride reacts with water to

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(62) King, W. R., and J. K. Ferrell. Fluoride Emissions from Phosphoric Acid Plant Gypsum Ponds. EPA-650/2-74-021, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1974. 329 pp.

form fluosilicic acid and silica. The fact that these emissions are insoluble in water partially explains their existence in the scrubbed vapor streams.

Source test measurements for particulate emissions range from 0.0011 to 0.17 g/kg P_2O_5 as shown in Appendix B. The average emission factor is 0.054 g/kg P_2O_5 ± 164% based on data from five plants representing 16% of total U.S. production.

c. Sulfur Oxides--
The origin of SO_x emissions in WPPA manufacture is not clear. The emissions can result from dissolved sulfur dioxide in the sulfuric acid or from reactions of the phosphate rock with sulfuric acid (12). These gases are rarely measured at acid plants.

Data from a Public Health Service document (12) and from one plant reporting SO_x emissions (Appendix B) gave a range of emission factors of 0.0077 to 0.058 g/kg P_2O_5 (see Appendix B). An average of these figures gives an emission factor of 0.032 g/kg P_2O_5 ± 240%.

d. Phosphates--
Phosphate emissions consist of phosphate rock, various phosphates, and phosphoric acid mist. During particulate analysis of stack gases, all of these emission species are collected, with various efficiencies, on the filter paper.

Emissions data were obtained from one WPPA plant. In this series of three tests (Appendix B), the filter paper was removed and the particulates and gases were passed through three water-filled gas bubblers. The solution was then analyzed for total phosphorus content and reported as grams of P_2O_5 per kilogram of P_2O_5 produced.

Comparison of these three source test measurements at one plant with the range of total particulates emitted at the other plants indicates that approximately 80% of the particulate matter consists of water-soluble phosphorus compounds.

Because phosphate emissions are in particulate form, phosphate emission factors were not separately calculated; they are included with the particulate emission factor.

3. Gypsum Pond Emissions

Emissions of volatile fluorine, hydrogen fluoride, and silicon tetrafluoride from gypsum ponds have been the subject of numerous studies (20, 62-65). An EPA report (20) presents a critical review of the major studies reporting gypsum pond fluoride emissions.

After close scrutiny of the data, emissions from gypsum ponds were found to range from 11 to 1,100 kg F/(km²-day) [0.1 to 10 lb/(acre-day)] with an average value of 220 kg F/(km²-day). This results in an emission factor of 0.025 to 2.5 g F/kg of P_2O_5 for an average plant producing 486 metric tons of P_2O_5 with a typical gypsum pond of 1.11 km². The average emission factor is 0.50 g F/kg of P_2O_5 (20).

At the end of August 1977, a field program was carried out near Bartow, Florida, with the cooperation of EPA for measuring fluoride emissions from a gypsum pond (66). Average fluoride emission rates from the pond were estimated to be in the range of 440 to 1,100 kg F/(km²-day) [4 to 10 lb/(acre-day)]. Data collected by remote optical sensing indicate that fluoride emissions from the gypsum pond consisted entirely of hydrogen fluoride. The silicon tetrafluoride concentration was below the detectable threshold of 0.5 ppb. Results from this study, however, are still preliminary and may be subject to change in the final report.

4. Emission Summary

Emission factors and stack heights for WPPA manufacture are summarized in Table 20 for each emission point. The corresponding errors are based on the "Student t" test at 95% confidence (67). Data used to generate this table are presented in Appendix B.

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(63) English, M. Fluorine Recovery from Phosphatic Fertilizer Manufacture. Chemical Process Engineering, 48(12):43-47, 1967.

(64) Bowers, Q. D. Disposal as Waste Material--U.S. Practice. in: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 505-510.

(65) Huggstutler, K. K., and W. E. Starnes. Sources and Quantities of Fluorides Evolved with the Manufacture of Fertilizer and Related Products. Journal of the Air Pollution Control Association, 11(12):682-684, 1966.

(66) Preliminary Report: Remote Monitoring of Fluoride Emission from Gypsum Ponds. EPA-69/01-4145, Task 10, U.S. Environmental Protection Agency, Washington, D.C., November 1977. 35 pp.

(67) Volk, W. Applied Statistics for Engineers, Second Edition. McGraw-Hill Book Co., New York, New York, 1969. 110 pp.

TABLE 20. AVERAGE STACK HEIGHTS AND CONTROLLED EMISSION FACTORS FOR WET PROCESS PHOSPHORIC ACID AND SUPERPHOSPHORIC ACID PLANTS

Emission point	Stack height, m	Emission factor, g/kg P_2O_5		
		Total fluoride	Particulate	SO_x
Wet process phosphoric acid:				
Rock unloading	12	0	0.15 ± 250%	0
Rock transfer and conveying	21	0	0.045 ± 180%	0
Wet scrubber system:	29	0.010 ± 40%	0.054 ± 164%	0.032 ± 200%
Gypsum pond		0.025 to 2.5 avg 0.50	0	0
Superphosphoric acid:				
Wet scrubber	21	0.0073[a]	0.011 to 0.055	0

[a] Only two data points.

B. SUPERPHOSPHORIC ACID

The most popular process (at about 75% of existing plants) for dehydration of 54% P_2O_5 phosphoric acid to produce greater than 66% P_2O_5 superphosphoric acid involves the use of heat transfer surfaces. Although some (approximately 25%) manufacturers use submerged combustion, its large volume of effluent gases makes this process unattractive due to the cost of extensive scrubbing facilities. Expansion of this process is unlikely (31). Consequently, only vacuum evaporation processes are evaluated in this report.

Emission species from superphosphoric acid plants include fluorine compounds and particulates. Fluorine is evolved in the form of hydrogen fluoride. Particulates are limited to liquid phosphoric acid aerosols and mists produced by the condensation process. The falling film evaporator (see Section 3) can generate aerosols which are submicrometer in size (45).

Two plants for which fluorine emissions data were available use vacuum evaporation processes. The barometric condenser, hot well, and product cooling tank are vented to a two-state wet scrubber. Fluorine emission factors from these plants are 0.0036 and 0.011 g/kg P_2O_5, with an average value of 0.0073 g/kg P_2O_5 (Appendix B).

One plant reported particulate emissions ranging from 0.011 to 0.055 g/kg P_2O_5.

The average stack height for the plant emissions is 21 m (Appendix B). Emission factors and stack height for superphosphoric acid manufacture are included in Table 20.

C. NORMAL SUPERPHOSPHATE

Emission points at NSP production facilities include the mixer, den, and curing building. Emissions are also generated by materials storage and handling operations. A list of emission points at an average plant and corresponding emission species follows:

- Ground rock unloading and feeder system--particulate.
- Mixer and den--fluoride compounds and particulate.
- Curing building--fluoride compounds and particulate.

Particulate emissions from materials storage and handling operations result from unloading hopper-bottom railroad cars and transporting the ground phosphate rock to the superphosphate plant by screw conveyors, belt conveyors, and bucket elevators. Additional emissions issue from the product storage and curing building as a result of fertilizer handling and shipping operations within the building. Typical composition analyses of superphosphate fertilizers are given in Table 21 (13, 18, 20). Concentrations of radioactive elements in phosphate fertilizer products were reported in Table 4.

Fluorides enter the NSP production process in the phosphate rock and are released as a result of the acidulation reaction. During acidulation, the calcium fluoride content of the rock is attacked by the acid (sulfuric or phosphoric), resulting in formation of hydrofluoric acid. This in turn reacts with silica found in the rock to form silicon tetrafluoride which hydrolyzes to form fluosilcic acid. The reaction sequence leading to the formation of fluosilicic acid is given below:

$$\text{Phosphate rock} + \text{acid} \longrightarrow HF \qquad (18)$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \qquad (19)$$

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2 \qquad (20)$$

Some of the hydrogen fluoride and silicon tetrafluoride are volatilized during the process leading to fluoride emissions. Fluoride vapors that evolve as hydrogen fluoride and silicon tetrafluoride are released from the mixer, den, and curing building. Fluorine is also present as a constituent of the rock and fertilizer particulate matter. Between 1.5 kg and 9.0 kg of fluorides per metric ton of NSP (Appendix C) are relased during the production and curing operations. Emissions of fluoride and particulate from the mixer and den are controlled by scrubbing with water. Scrubber liquor may be recirculated pond water or a weak solution of fluosilicic acid. Nearly two-thirds of the NSP plants presently practice fluorine recovery, thereby eliminating or greatly reducing the need for a pond. No measurements are available for fugitive fluoride emissions from those NSP plants that make use of a pond system, but such emissions will be less than fluoride emissions from those gypsum ponds discussed in the section on WPPA manufacture.

TABLE 21. TYPICAL CHEMICAL COMPOSITION OF FLORIDA NORMAL SUPERPHOSPHATE AND TRIPLE SUPERPHOSPHATE FERTILIZER (13, 18, 20)

Component[a]	Expressed as	Units	NSP content[b]		TSP content[b]	
			Range	Average	Range	Average
Aluminum	Al_2O_3	percent	0.21 to 1.16	0.72	1.20 to 1.95	1.68
Arsenic	As	ppm	4.1 to 30.6	12.5	10.5 to 14.3	12.2
Ash (acid-insoluble)	Ash	percent	2.00 to 13.65	4.45	2.50 to 4.90	3.55
Boron	B	ppm	<3 to 30	11	29 to 115	80
Calcium, total	CaO	percent	27.20 to 31.13	29.52	16.60 to 21.57	19.65
Calcium, water soluble	CaO	percent	10.19 to 14.90	13.10	14.60 to 16.80	
Carbon, organic	C	percent	0.21 to 0.27	0.24		
Carbon dioxide	CO_2	percent	0 to 0.44	0.066	0 to 0.22	0.11
Chlorine	Cl	percent	–[c]	0.80	<0.1	
Chromium	Cr	ppm	70 to 72	71	0 to 890	513
Cobalt	Co	ppm	0 to 2.8	1.3	2.4 to 4.8	3.4
Copper	Cu	ppm	28 to 64	47	3 to 22	11
Fluorine	F	percent	1.41 to 2.15	1.74	2.00 to 3.49	2.47
Free acid	H_3PO_4	percent	1.30 to 2.15	1.71	0.19 to 3.85	2.6
Free acid-free water ratio	H_3PO_4/H_2O		0.12 to 1.19	0.58	0.06 to 1.59	0.8
Iodine	I	ppm	16 to 50	33		
Iron	Fe_2O_3	percent	0.38 to 1.37	0.67	0.92 to 2.00	1.59
Lead	Pb	ppm	8 to 20	14	0 to 65	26
Lithuim	Li	ppm	–[c]	2		
Magnesium, total	MgO	percent	0.04 to 0.12	0.07	0.05 to 1.00	0.38
Magnesium, water soluble	MgO	percent	–[c]	0.03		
Manganese	Mn	ppm	65 to 95	77	110 to 300	214
Molybdenum	Mo	ppm	–[c]	1.6	3.7 to 16.8	8.0
Nitrogen	N	percent	–[c]	0.1	0.06 to 0.40	0.26
Phosphorus, total	P_2O_5	percent	16 to 21	20	45 to 49	48
Potassium	K_2O	percent	0.16 to 0.24	0.20	0 to 0.57	0.35
Selenium	Se	ppm	0 to 1.5	0.6	–[c]	<0.8
Silicon	SiO_2	percent	4.00 to 4.54	4.35	0.60 to 7.37	4.42
Silver	Ag	ppm	15 to 20	18		
Sodium	Na_2O	percent	0.09 to 0.13	0.11	0.13 to 1.79	0.97
Sulfur, total	SO_3	percent	26.58 to 30.55	28.99	2.12 to 4.95	3.01
Sulfur, water soluble	SO_3	percent	6.37 to 13.49	10.67	1.65 to 5.77	2.98
Titanium	Ti	ppm	54 to 270	162	0 to 599	300
Vanadium	V	ppm	20 to 71	46	0 to 3,875	2,515
Water, reported as "moisture"	H_2O	percent	2.3 to 8.3	5.64	0.87 to 6.30	3.4
Water, free	H_2O	percent	1.09 to 5.71	3.65	0.88 to 4.42	2.57
Water of crystallization	H_2O	percent	2.44 to 5.14	3.55	1.29 to 6.26	3.47
Zinc	Zn	ppm	50 to 200	134	0 to 320	102

[a] Radium, uranium and thorium are reported in Table 4.

[b] Blanks indicate component not analyzed.

[c] Average based on one to two measurements.

Source test data from fertilizer plants were collected from published literature and sampling data on file as of October 1976 at the Florida Department of Environmental Regulation in Winter Haven. Raw data used to establish emission factors are given in Appendix B.

Emission factors for the emission species at NSP plants as a function of emission point are shown in Table 22. Emission factors for the mixer-den and the curing building were calculated by averaging the appropriate values in Appendix B. Data were available for only one set of four tests for controlled fluoride emissions from the product curing building. Because most (more than 85%) curing buildings remain uncontrolled, the fluoride emission factors were normalized to uncontrolled emissions using the fluoride control efficiency of 97% reported by Plant A. The low volumes of fertilizer materials handled by these storage facilities and the decline in industry production levels for NSP make control devices economically impractical.

TABLE 22. EMISSION FACTORS FOR AN AVERAGE NSP PLANT BASED ON CONTROLLED EMISSION SOURCES

Emission source	Emission factor, g/kg P_2O_5	
	Particulates	Fluorides[a]
Rock unloading	0.28[b]	-[c]
Rock feeding	0.055 ± 180%	-[c]
Mixer and den	0.26 ± 86%	0.10 ± 120%
Curing building[d]	3.6[b]	1.9 ± 120%

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore 95% confidence limits could not be determined.

[c] Not emitted from this source.

[d] Uncontrolled emission factors since curing building emissions are not controlled at an average plant.

Particulate emissions due to the rock unloading, storage, and transfer operations and the fertilizer handling and shipping activities occurring in the product curing building were not available for NSP plants. Emission factors for the rock unloading and storage activities and for the ground rock weighers and feeders are developed in Appendix B from emission factors for similar activities occurring at GTSP production facilities. In order to obtain an estimate of the particulate emissions arising from fertilizer handling and shipping operations occurring in the curing building, two measurements for controlled particulate emissions from the combined shipping, screening, and milling of ROP-TSP were used (Appendix B).

Error limits shown in Table 22 and developed in Appendix B were established by applying a "Student t" test to the input data (66). The "t" test is applied because the sample sizes are fewer than 30 in number and thus may not be normally distributed. The statistical data used to establish the error limits are shown in Appendix B.

As an aid in determining the reliability of reported fluorine emission measurements, mass balances are developed in Appendix C for the production of NSP. Between 7.5 g F/kg P_2O_5 and 45 g F/kg P_2O_5 (depending on the fluoride concentration of the NSP product) are released during the production and curing operations. Based on data from the Florida Department of Environmental Regulation, a scrubber control efficiency of 99% for fluoride removal was used. Controlled fluoride emissions would then range from 0.07 g F/kg P_2O_5 to 0.45 g F/kg P_2O_5. This compares favorably with our values of 0.1 g F/kg P_2O_5 and 0.05 g F/kg P_2O_5 developed for controlled emissions from the mixer-den and curing building, respectively (Table 22).

D. TRIPLE SUPERPHOSPHATE

1. Run-of-the-Pile Triple Superphosphate

The process for production of ROP-TSP is similar to that for NSP. Emission points and emission species therefore closely resemble those from NSP production facilities; namely,

- Ground rock unloading and feeder system--particulate.
- Mixer and den--fluoride compounds and particulate.
- Curing building--fluoride compounds and particulate.
- Gypsum pond--fluoride compounds.

TSP manufacture differs from that of NSP in that WPPA is used for acidulation in place of sulfuric acid. As a result, fluorides enter the TSP production process not only as a constituent of the rock but also as an impurity in the phosphoric acid.

Emissions of fluorides are controlled by wet scrubbers that discharge a fluoride-containing wastewater stream to holding ponds. Water in the ponds is recycled for use in the scrubbers. Gaseous fluoride is also emitted from the ponds used as reservoirs to hold contaiminated scrubber water. The development of emission factors for the gyspum ponds is covered under WPPA manufacture, and will therefore not be considered here.

Emission factors for the emission species from ROP-TSP plants are given in Table 23. The raw data used to compile these factors are presented in Appendix B.

TABLE 23. EMISSION FACTORS FOR AN AVERAGE ROP-TSP PLANT BASED ON CONTROLLED EMISSION SOURCES

Emission source	Emission factor, g/kg P_2O_5	
	Particulates	Fluorides[a]
Rock unloading	0.07[b]	–[c]
Rock feeding	0.014 ± 170%	–[c]
Cone mixer, den, curing building	0.16 ± 50%	0.10 ± 40%

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore 95% confidence limits could not be calculated.

[c] Not emitted from this source.

The fluoride emission factor in Table 23 was averaged from source test data available for Plants A and B, Appendix B. Fluoride emissions data from Plant C did not take into account emissions from the curing building and were not included in the averaging procedure. Emissions from the mixer, den, and curing building at a typical plant are vented to a common stack; therefore, individual emission factors for each source were not developed.

In order to estimate particulate emissions for mixing-denning-curing-shipping operations, source test data for mixing-denning and screening-milling at Plant C (Appendix B) were utilized. Particulate emissions data from fertilizer screening and milling operations were used in deriving the curing building emission factor, because these activities represent the major source of particulates from a curing building. Particulate emission factors for the ground rock unloading and transfer operations were developed from Appendix B using emission factors for similar activities occurring at GTSP production facilities.

An estimated 8 g F/kg P_2O_5 are released during the production and curing of ROP-TSP. This value is based on a material balance developed in Appendix C. A scrubber efficiency of 99% would result in a controlled emission factor of 0.08 g F/kg P_2O_5. This value can be compared to the average controlled emission factor of 0.10 g F/kg P_2O_5 based on actual source tests.

2. Granular Triple Superphosphate

Five plant operations release emissions at TSP plants using the Dorr-Oliver direct granulation process. They are described in detail in Section 3. The emission points and the emission species associated with each are as follows:

- Ground rock unloading and feeder system--particulate.
- Reactor and granulator--fluoride compounds and particulate.
- Dryer and cooler--SO_x, fluoride compounds, and particulates.
- Screens and oversize mills--particulate.
- Storage and shipping--fluoride compounds and particulate.

Fluorides enter the TSP process in the phosphate rock and the WPPA and are volatilized and evolved during the acidulation reaction. Evolution of fluoride vapors continues throughout the manufacturing process and during storage as the reaction proceeds to near completion. Emissions of fluorides are in the form of the water-soluble gases, silicon tetrafluoride, and hydrogen fluoride. Fluorine is also released as a constituent of the rock and fertilizer particulate matter.

An estimated 7 g of fluoride vapors per metric ton of GTSP (Appendix B) are released during production and curing. The control of fluoride emissions is accomplished by scrubbing the exhaust gas streams with recycled pond water. Fluoride emissions from gypsum ponds are considered in the section on the manufacture of WPPA.

In addition to fluoride compounds and dust particles, the dryer exhaust contains SO_x. These emissions result from the combustion of fuel oil containing sulfur.

To calculate emission factors, source test data from GTSP plants were collected from published literature and sampling data on file at the Florida Department of Environmental Regulation in Winter Haven. The raw data used to establish emission factors are given in Appendix B.

Emission factors at GTSP plants as a function of emission point are shown in Table 24. Emissions from the reactor, granulator, dryer, cooler, screens, and mills at an average plant are vented to a common stack. As a result, individual emission factors were not developed for separate segments of the production process.

There are no source test data for SO_x emissions from the dryer. Estimates of uncontrolled SO_x emissions were calculated by Plants A and E (Appendix B) on the basis of fuel oil consumption and sulfur content.

A check on the reliability of fluoride emission measurements can be made by comparing the estimated fluoride release based on a mass balance. On this basis (Appendix C), an estimated 15.2 g F/kg P_2O_5 are released during the production and curing of GTSP. A scrubber efficiency of 99% would result in a controlled emission factor of 0.152 g F/kg P_2O_5. This can be compared with the

TABLE 24. EMISSION FACTORS FOR AN AVERAGE GTSP PLANT BASED ON CONTROLLED EMISSION SOURCES

Emission source	Emission factor, g/kg P_2O_5		
	Particulates	Fluorides[a]	SO_x
Rock unloading	0.09[b]	–[c]	–[c]
Rock feeding	0.017 ± 180%	–[c]	–[c]
Reactor, granulator, dryer, cooler, screens	0.05 ± 320%	0.12 ± 30%	1.86[d]
Curing building	0.10 ± 240%	0.018 ± 40%	–[c]

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore, 95% confidence limits could not be calculated.

[c] Not emitted from this source.

[d] Worst case estimate based on fuel oil sulfur content.

controlled emission of 0.156 g F/kg P_2O_5 developed by adding average measured values of 0.099 g F/kg and 0.57 g F/kg from the reactor-den and curing building, respectively.

E. AMMONIUM PHOSPHATES

Air emissions from production of ammonium phosphate fertilizers by ammoniation-granulation of phosphoric acid and ammonia result from six process operations. Emission sources and their related emission species are:

- Reactor--ammonia, fluorides.
- Ammoniator-granulator--ammonia, fluorides, particulates.
- Dryer--ammonia, fluorides, particulates, combustion gases.
- Cooler--ammonia, fluorides, particulates.
- Product sizing and material transfer--particulates.
- Gypsum pond--fluorides.

Ammonia emissions are volatilized from the reactor and ammoniator-granulator due to incomplete chemical reactions and excess free ammonia. Ammonia emitted from the dryer and cooler is due to dissocation of fertilizer product. Particulate emissions result from entrainment of MAP and DAP dusts in ventilation air streams. Particulate emission species may also include ammonium fluoride and ammonium fluosilicates (45).

Fluoride emissions originate from the fluoride content of phosphoric acid. Air emissions are formed based on the following set of equilibrium reactions:

$$H_2SiF_6 \rightleftarrows 2\ HF + SiF_4 \qquad (21)$$

$$4\ HF + SiO_2 \rightleftarrows H_2O + SiF_4 \qquad (22)$$

At operating temperatures associated with MAP and DAP production, emissions of silicon tetrafluoride are favored over hydrogen fluoride (45).

Dryer offgases contain natural gas or fuel oil combustion products. EPA found combustion product pollutants in such minor concentrations that they were dismissed from consideration during EPA's development of background information for air standards for the phosphate fertilizer industry (31). Therefore, these emission species will not be considered further in this study.

Emissions from the first five emission points reach the atmosphere through a stack, while gypsum pond emissions are fugitive. Although there are six emission sources, there may be fewer emission points because some plants combine flue gases from multiple sources for subsequent emission control.

Emission factors were developed for air emission species from each emission point from data in published literature and from sampling data on file at the Florida Department of Environmental Regulation, Winter Haven, Florida. Raw data used to calculate emission factors were compiled and are presented in Appendix B. Emission factors are reported in the literature in units of grams per kilogram of P_2O_5 input, grams per kilogram of P_2O_5 output, and grams per kilogram of product. All P_2O_5, except losses due to emissions, is assumed to reach the product. Therefore, input and output emission factors are equivalent. For those emission factors expressed as grams per kilogram of product, a 46% P_2O_5 content was assumed. All emission factors developed for this study are expressed in units of grams per kilogram of P_2O_5.

Emission factors presented in Table 25 were calculated by averaging appropriate values from Appendix B. Due to the nature of both emissions data and pollution control practices at plants, emissions from the reactor and ammoniator-granulator were combined and reported as from one emission point. Dryer and cooler emissions were treated in the same manner. Table 25 also shows 95% confidence intervals associated with each emission factor as calculated by the "Student t" method.

As Appendix B indicates, 53% of the raw data are from plants which collectively report all air emissions as "total plant" emissions. Therefore, total plant emission factors were calculated from these data and are also shown in Table 25. Because emission factors for individual emission species from the three process-related emission points are similar in magnitude to those reported as total plant emissions, a total plant emission factor for each emissions species was calculated from all data in Appendix B according to the following equation:

$$E_{Total} = \frac{\left(E_{R/A} + E_{D/C} + E_P\right)\left(N_{R/A} + N_{D/C} + N_P\right) + E_{TP}\ N_{TP}}{N_{R/A} + N_{D/C} + N_P + N_{TP}} \qquad (23)$$

TABLE 25. EMISSION FACTORS DEVELOPED FROM SOURCE TEST DATA GIVEN IN APPENDIX B

	Controlled emission factors	
Emission point[a]	Mean, g/kg P_2O_5	95% Confidence interval, % of mean
Reactor/ammoniator-granulator:		
Fluoride (as F)	0.023	±80
Particulate	0.76	±90
Ammonia	-[b]	-[b]
Dryer/cooler:		
Fluoride (as F)	0.015	±160
Particulate	0.75	±60
Ammonia	-[b]	-[b]
Product sizing and material transfer:		
Fluoride (as F)	0.001	-[c]
Particulate	0.03	-[c]
Ammonia	-[b]	-[b]
Reported as total plant emissions:		
Fluoride (as F)	0.038[d]	±30
Particulate	0.15[e]	±120
Ammonia	0.068	±75

[a] Fugitive emissions are included in the text.

[b] No information available; although ammonia is emitted from these unit operations, it is reported as a total plant emission.

[c] Emission factor represents only 1 sample.

[d] A fluoride emission guideline of 0.03 g/kg P_2O_5 input has been promulgated by EPA (47).

[e] Based on limited data from only 2 plants.

where $E_{R/A}$, $E_{D/C}$, E_P, and E_{TP} are emission factors from raw data for the reactor/ammoniator-granulator, dryer/cooler, product sizing and material transfer, and total plant, respectively. $N_{R/A}$, $N_{D/C}$, N_P, and N_{TP} are the corresponding number of samples used to generate each emission factor. This calculation results in the following total plant stack emission factors:

Particulates: 1.5 g/kg P_2O_5 ± 69%[a]

Fluoride (as F): 0.038 g/kg P_2O_5 ± 30%[b]

Ammonia: 0.068 g/kg P_2O_5 ± 75%

Information on fluoride emissions from the gypsum pond is reported in the section on WPPA manufacture. One-half of the 48 ammonium phosphate plants are located at fertilizer complexes producing WPPA. No measurements are available for fugitive

fluoride emissions from ponds located at plants producing only ammonium phosphates. However, pond systems at ammonium phosphate plants not located at fertilizer complexes are proportionately smaller and would have lower fluoride emissions than those at complexes.

F. POTENTIAL ENVIRONMENTAL EFFECTS

The source assessment program employs certain criteria to help evaluate the relative impacts of the source types studied. These parameters are source severity, affected population, state and national emission burdens, and growth factor. In evaluating potential environmental effects, average parameters have been employed (e.g., emission factors, stack heights, population densities). A more detailed plant-by-plant evaluation was beyond the scope of the project and conclusions are not drawn with regards to actual environmental impacts at specific plant sites.

1. Source Severity

Source severity compares the time-averaged maximum ground level concentration of an emitted pollutant, $\overline{X}_{max}$, to an estimated hazard factor, F (Equation 24).

$$S = \frac{\overline{X}_{max}}{F} \tag{24}$$

The hazard factor, F, is defined as the primary ambient air quality standards presently exist for particulates, sulfur oxides (SO_x), nitrogen oxidants (NO_x), carbon monoxide (CO), hydrocarbons,[c] and oxidants. For noncriteria emission species (fluoride and ammonia), F is derived from the threshold limit value (TLV®)

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[a] Estimated uncertainty based on process-related emissions.

[b] Estimated uncertainty based on total plant emissions.

[c] The value of 160 μg/m³ used for the primary ambient air quality standard for hydrocarbons in this report is a recommended guideline for meeting the primary ambient air quality standard for photochemical oxidants.

for the chemical substance (68) as TLV (8/24)(1/100). The factor 8/24 corrects for 24-hr exposure and 1/100 is a safety factor. In the calculation of source severity a conservative safety factor is used due to the lack of definitive health effects data.

The time-averaged maximum downwind ground level concentration of each emission species is given by (69):

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \tag{25}$$

where

$$\chi_{max} = \frac{2\ Q}{\pi e \bar{u} h^2} \tag{26}$$

and χ_{max} = short-term (i.e., 3 min) maximum ground level concentration, g/m^3

t_o = instantaneous averaging time, 3 min

t = averaging time, 1,440 min

Q = emission rate, g/s

π = 3.14

e = 2.72

$\bar{u}$ = average wind speed, m/s

h = stack height, m

For criteria pollutants, the averaging time, t, is the same as that for the corresponding ambient air quality standard. For noncriteria emission species, t is 1,440 min (24 hr). A wind speed of 4.5 m/s is used for $\bar{u}$.

The equation for χ_{max} (Equation 26) is derived from the general plume dispersion equation for an elevated source (69). For fugitive emissions occurring at ground level (i.e., from materials handling operations or from the gypsum pond), a special form of the Gaussian plume dispersion equation is developed, taking the following form (69, 70):

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(68) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

(69) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1969. 62 pp.

(70) Reznik, R. B. Source Assessment: Flat Glass Manufacturing Plants. EPA-600/2-76-032b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 147 pp.

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z \bar{u}} \qquad (27)$$

where χ = ground level downwind pollutant concentration, g/m^3
σ_y = 0.2089 $x^{0.9031}$
σ_z = 0.113 $x^{0.911}$
Q = emission rate, g/s
π = 3.14
$\bar{x}$ = average wind speed, m/s
x = radial distance downwind from the source, m

Values of x are then calculated to determine at what distance downwind from the source the severity falls below 0.05 and 1.0 for an average emission factor.

The 24-hr ambient air quality standards of 260 µg/m^3 for particulates and 365 µg/m^3 for SO_x were used as hazard factors to calculate source severities. For fluoride emissions, a TLV of 2.0 mg/m^3 (based on hydrogen fluoride) was used to calculate F for use in source severity calculations. The corresponding TLV for ammonia is 18 mg/m^3 (68).

The source severity calculation does not consider the distance at which maximum ground level concentrations of an emitted pollutant occurs. In some cases, depending on individual plant layouts, the point of maximum severity may occur within plant boundaries. As mentioned earlier this parameter is used as a basis for comparing a large number of emission sources, and a detailed plant-by-plant analysis was not conducted.

a. Phosphoric Acid and Superphosphoric Acid Plants--

Values for $\bar{\chi}_{max}$ and S were calculated for each emission point at an average plant. These values are presented in Table 26. Source severities were also calculated for each plant based on average emission factors and stack heights. Plant production rates used in severity calculations were derived for phosphoric acid and superphosphoric acid plants by multiplying plant capacity data in Appendix A by utilization factors of 0.70 and 0.49, respectively, obtained by dividing 1975 annual productions by available industry capacities. The resulting severity distributions are presented in Figures 34, 35, and 36 for particulate emissions from rock handling operations at WPPA plants, for particulate and fluoride emissions from the wet scrubber at WPPA plants, and for fluoride emissions from superphosphoric acid plants, respectively. Each severity distribution is plotted as cumulative percent of the number of plants versus severity for each emissions species from each emission point.

Source severity distributions were not calculated for SO_x emissions from the wet scrubber at WPPA plants or for particulate emissions from superphosphoric acid plants because of the smaller amount of emissions data.

TABLE 26. VALUES FOR $\bar{\chi}_{max}$ AND SOURCE SEVERITIES FOR EMISSIONS FROM AN AVERAGE WET PROCESS PHOSPHORIC ACID AND SUPERPHOSPHORIC ACID PLANT

	$\bar{\chi}_{max}$, µg/m³			Source severity		
Emission point	Total fluoride	Particulate	SO_x	Total fluoride	Particulate	SO_x
Wet process phosphoric acid:						
Rock unloading	0[a]	106	0	0[a]	0.41	0
Rock transfer and conveying	0	10.4	0	0	0.040	0
Wet scrubber system	1.2	6.5	3.9	0.18	0.025	0.011
Gypsum pond	-[b]	0	0	-[b]	0	0
Superphosphoric acid:						
Wet scrubber	0.55	2.5	0	0.09	0.01	0

[a] Zero indicates this species is not emitted from this source.

[b] Not applicable.

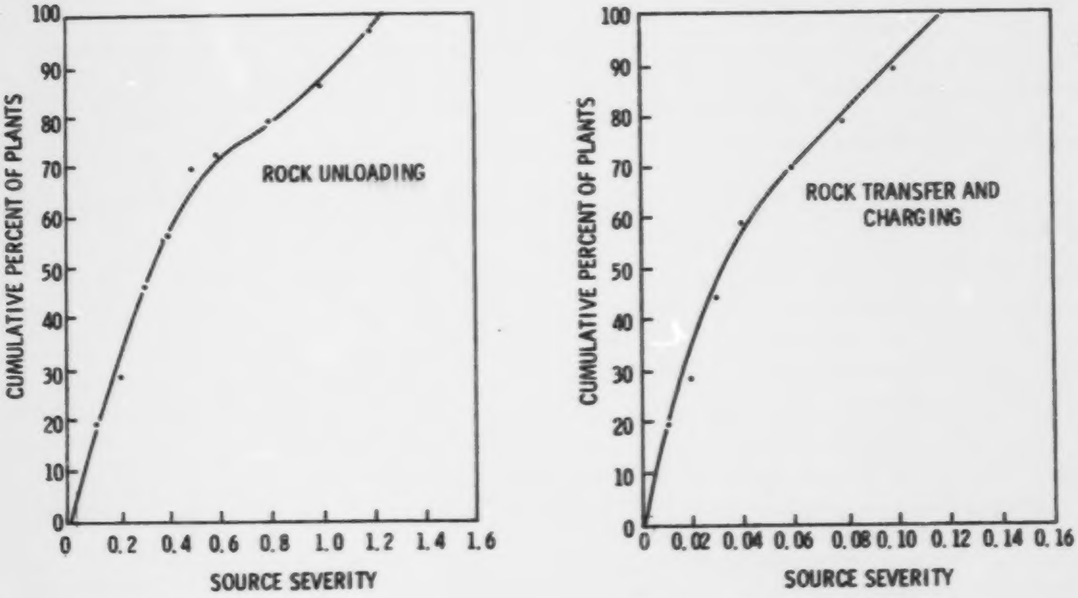
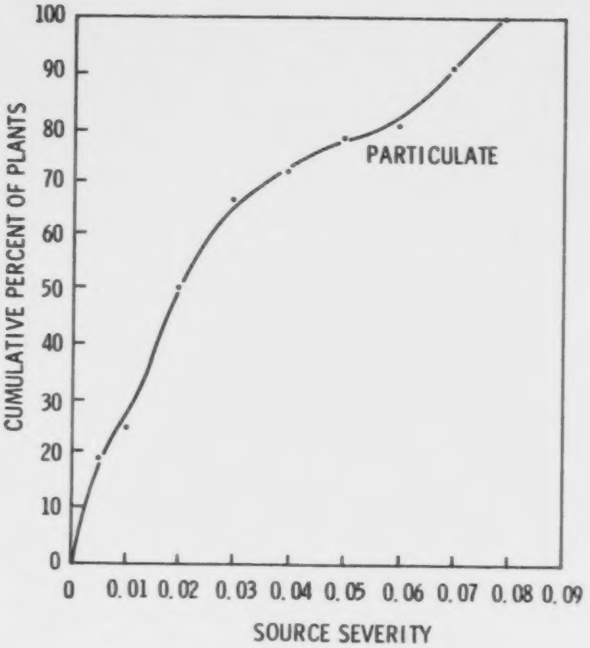


Figure 34. Source severity distribution of particulate emissions from rock handling operations at WPPA plants.



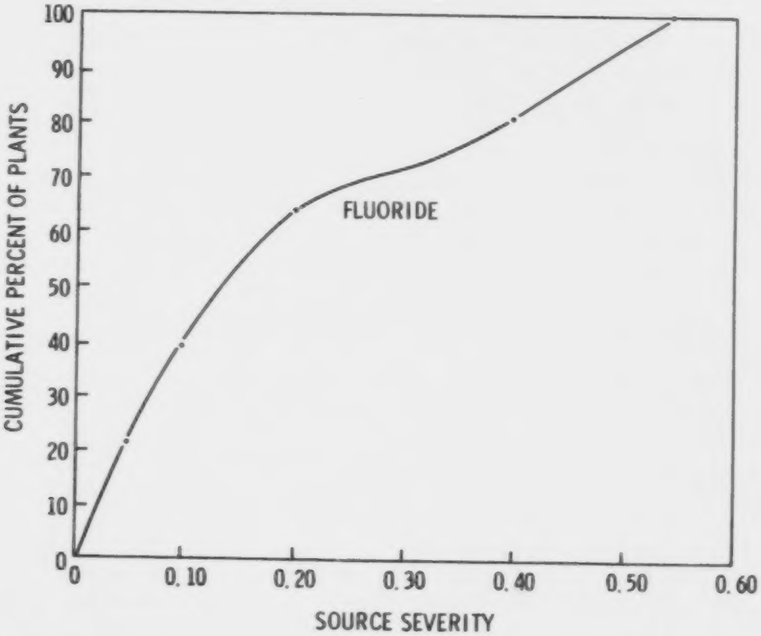


Figure 35. Source severity distribution of particulate and fluoride emissions from the wet scrubber at WPPA plants.

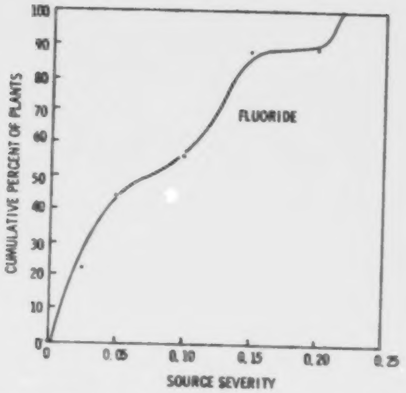


Figure 36. Source severity distribution of fluoride emissions from superphosphoric acid plants.

Because no stack height is associated with fluoride emissions from gypsum ponds, source severity had to be calculated differently. From Equations 25 and 27 and for 24-hr averaging times, the value of $\overline{\chi}$ divided by F yielded the graph shown in Figure 37. Dashed lines give the change in $\overline{\chi}/F$ with distance from the center of a typical gypsum pond for emission rates of 11 and 1,100 kg F/(km²-day) [0.1 and 10 lb/(acre-day)]. The solid line is for an average emission factor of 220 kg F/(km²-day). Fluoride emissions from the gypsum pond are treated as a point source located at the center of the pond and represent a worst case analysis. Note that the value of $\overline{\chi}/F$ falls below 1.0 at approximately 1300 m from the center of the pond for an average emission rate, and it falls below 0.05 at approximately 6700 m. A severity distribution for fluoride emissions from the gypsum pond at individual WPPA plants is presented in Figure 38, based on an average emission factor. Table 27 presents severity ranges for each species and emission point and also shows the percentage of plants having a source severity exceeding 0.05 and 1.0.

b. Normal Superhphosphate and Triple Superphosphate Plants--Table 28 presents the values of $\overline{\chi}_{max}$ and S for each emission point and for each emission species from three average superphosphate plants. Values are based on the current level of emission control at these plants.

Average stack heights in Table 28 were developed from stack heights for individual plants reported in Appendix B. A stack height of 15 m was determined from plant data for emissions from the baghouses controlling rock unloading and transfer operations. Emissions from the NSP curing building at an average plant are not controlled; they are exhausted from the building by ducts along one side. The height of the curing building, 12 m, was therefore used as the stack height for this source.

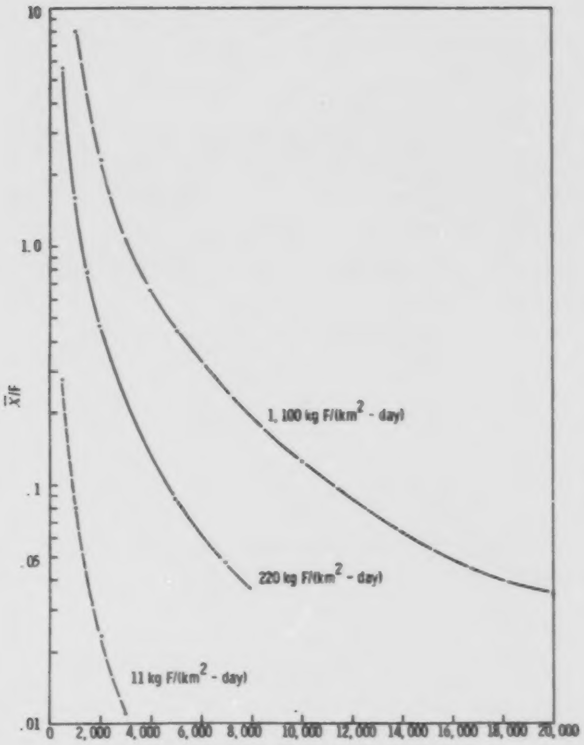


Figure 37. $\overline{\chi}/F$ as a function of radial distance downwind from gypsum pond.

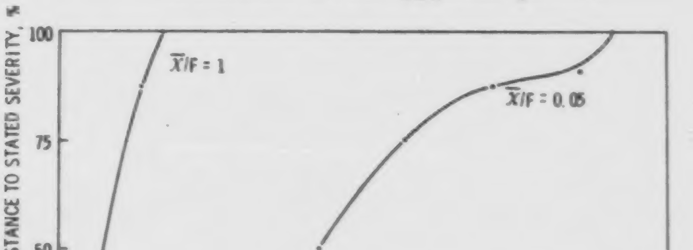


Figure 38. Distribution of distance to stated severity for fluoride emissions from the gypsum pond at WPPA plants.

TABLE 27. RANGE OF SOURCE SEVERITIES AND PERCENTAGE OF WET PROCESS PHOSPHORIC ACID AND SUPERPHOSPHORIC ACID PLANTS HAVING SEVERITIES GREATER THAN 0.05 OR 1.0

Emission point	Species	Source severity, S Minimum	 Maximum	Percentage of plants $S > 0.05$	 $S > 1.0$
Wet process phosphoric acid:					
Rock unloading	Particulate	0.011	1.26	86	14
Rock transfer and conveying	Particulate	0.001	0.12	28	0
Wet scrubber system	Particulate	<0.001	0.078	19	0
	Total fluoride	0.005	0.56	78	0
	SO_x	<0.001	0.01	–[a]	–[a]
Superphosphoric acid:					
Wet scrubber	Particulate	<0.001	<0.001	–[a]	–[a]
	Total fluoride	0.01	0.32	65	0

[a] Distribution was not calculated because of the small amount of emissions data available.

TABLE 28. MAXIMUM GROUND LEVEL CONCENTRATIONS AND SOURCE SEVERITIES OF CONTROLLED EMISSION SPECIES FROM AVERAGE SUPERPHOSPHATE PLANTS

Emission source category	Average stack height, m	$\overline{X}_{max}$, µg/m³ Fluoride	 SO_x as SO_2[a,b]	 Particulate	S Fluoride[c]	 SO_x as SO_2[a,b]	 Particulate[b]
NSP plants:							
Rock unloading	15	–[d]		4.9			0.02
Rock feeders	15			1.0			0.004
Mixer and den	18	1.2		3.0	0.18		0.01
Curing building[e]	12	50		92	7.2		0.35
GTSP plants:							
Rock unloading	15			16			0.062
Rock feeders	15			3.0			0.012
Reactor, granulator, screen, cooler, dryer	44	2.5	39	1.1	0.36	0.11	0.0042
Curing building	30	0.81		4.6	0.12		0.018
ROP-TSP plants:							
Cone mixer, den, storage building	26	5.3		8.1	0.77		0.031
Rock feeders	15			2.2			0.009
Rock unloading	15			11			0.042

[a] For worst case analysis, based on uncontrolled emission factor.

[b] Primary ambient air quality 24-hr standard for particulates equals 0.26 mg/m³; for SO_x it equals 0.365 mg/m³.

[c] TLV equals 2.0 mg/m³; F equals 6.7 µg/m³. [d] Blanks indicate emission species not emitted from the source category.

[e] Uncontrolled emissions.

To complement the source severity values based on plants representative of the industry, source severity distributions for the whole industry were calculated for all species emitted from each emission point. Plant production rates used in severity calculations were derived by multiplying plant capacity data in Appendix A by utilization factors of 0.66 and 0.65 for normal superphosphate and triple superphosphate plants, respectively, obtained by dividing 1975 productions by available industry capacities. Where actual stack heights were unknown, the average stack heights shown in Table 28 were used. A graphic representation of this result is shown in Figure 39, presented as the cumulative percent of plants with a source severity less than a specific value. Those emission points and associated emission species not illustrated in Figure 39 had source severities for all plants less than 0.01. Table 29 presents severity ranges for each species and each emission point and also shows the percentage of plants having a source severity exceeding 0.05 and 1.0.

Because no source test data were available for SO_x emissions from the dryer at GTSP plants, an emission factor was developed based on fuel analysis and consumption. Values of $\overline{\chi}max$ and S for SO_x emissions are based on a worst case analysis assuming no control, even though some control results when effluent gas streams are scrubbed by acidic pond water before discharge.

c. Ammonium Phosphate Plants--

Table 30 presents values for $\overline{\chi}_{max}$ and source severity for stack emissions from an average plant. Although some plants have multiple emission points, this evaluation sums all stack emission factors and assumes a single emission point having a stack height of 24 m. This simplification can be justified by examining the variation in stack heights from individual emission points in Table 31 (71). Variation in stack heights between emission points is well within one standard deviation of the mean.

In order to illustrate potential environmental impact of air emissions from the entire industry, source severity distributions were calculated and are presented in Figures 40 through 42.

Table 32 presents severity ranges for each species and each emission point and also shows the percentage of plants having a source severity exceeding 0.05 and 1.0.

2. Total Emissions

Potential environmental effects of the emissions from phosphate fertilizer plants can also be evaluated by determining the total

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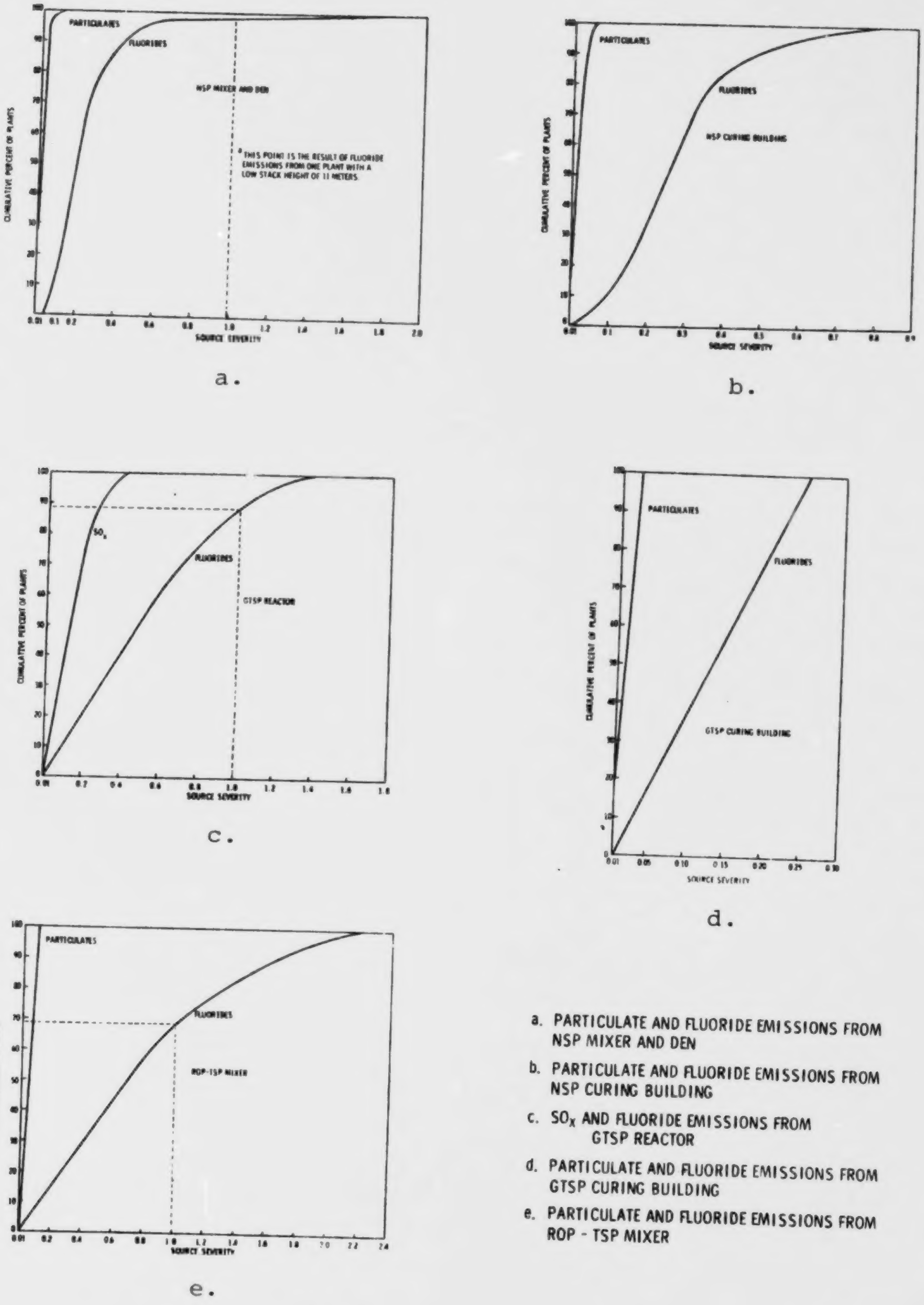
(71) National Emissions Data System Point Source Listing. SCC 3-01-030-01, 3-01-030-02, 3-01-030-99, 1976. 190 pp.



a.

b.

c.

d.

e.

a. PARTICULATE AND FLUORIDE EMISSIONS FROM NSP MIXER AND DEN

b. PARTICULATE AND FLUORIDE EMISSIONS FROM NSP CURING BUILDING

c. SO_x AND FLUORIDE EMISSIONS FROM GTSP REACTOR

d. PARTICULATE AND FLUORIDE EMISSIONS FROM GTSP CURING BUILDING

e. PARTICULATE AND FLUORIDE EMISSIONS FROM ROP - TSP MIXER

Figure 39. Cumulative source severity distributions.

TABLE 29. RANGE OF SOURCE SEVERITIES AND PERCENTAGE OF PLANTS HAVING SEVERITIES GREATER THAN 0.05 OR 1.0

Emission point	Species	Source severity		Percentage of plants	
		Minimum	Maximum	S > 0.05	S > 1.0
NSP:					
Rock unloading	Particulate			0	0
Rock feeding	Particulate			0	0
Mixer and den	Particulate	0.0036	0.13	3	0
	Fluoride	0.054	1.93	100	2
Curing building	Particulate	0.0046	0.057	2	0
	Fluoride	0.011	0.82	95	0
ROP-TSP:					
Rock unloading	Particulate			0	0
Rock feeding	Particulate			0	0
Cone mixer, den, curing building	Particulate	0.0065	0.093	30	0
	Fluoride	0.16	2.28	100	60
GTSP:					
Rock unloading	Particulate			0	0
Rock feeding	Particulate			0	0
Reactor, granulator, dryer, cooler, screens	Particulate			0	0
	Fluoride	0.063	1.45	100	12
	SO_x	0.018	0.41	76	0
Curing building	Particulate	0.0038	0.035	0	0
	Fluoride	0.027	0.25	85	0

NOTE.—Blanks indicate that the source severity for all plants is less than 0.01.

TABLE 30. MAXIMUM GROUND LEVEL CONCENTRATION AND SEVERITY FOR AN AVERAGE DAP PLANT

Stack emissions from total plant			
Species	TLV, mg/m³	$\bar{\chi}_{max}$, μg/m³	S
Fluoride (as F)	2.0	2.9	0.44
Particulate	0.26[a]	110	0.43
Ammonia	18	5.2	0.09

[a] Primary ambient air quality standard.

TABLE 31. VARIATION IN EMISSION SOURCE STACK HEIGHTS (71)

Source	Mean stack height, m	Standard deviation, m
Ammoniation-granulation	25[a]	9.4
Cooler/dryer	23[b]	9.3
Combined all stack height data	24	9.3

[a] Average of 49 stack heights.

[b] Average of 51 stack heights.

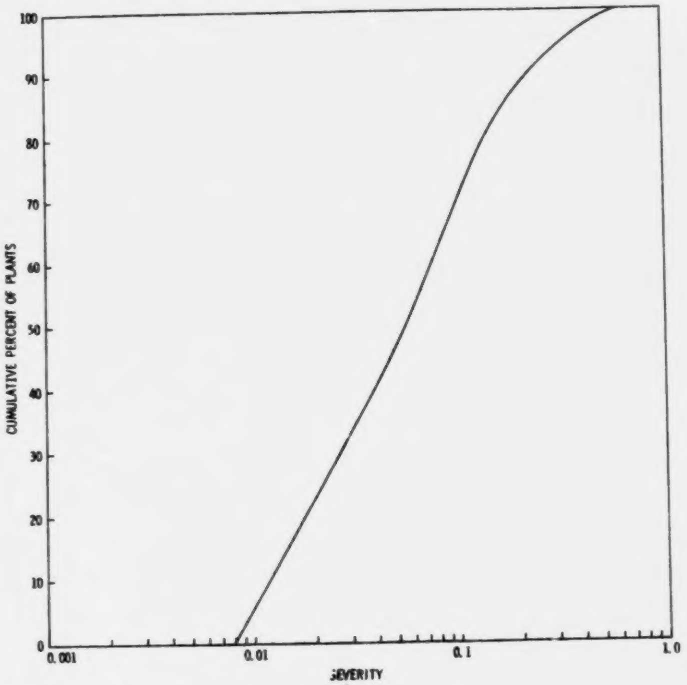


Figure 40. Severity distribution for total plant ammonia emissions.

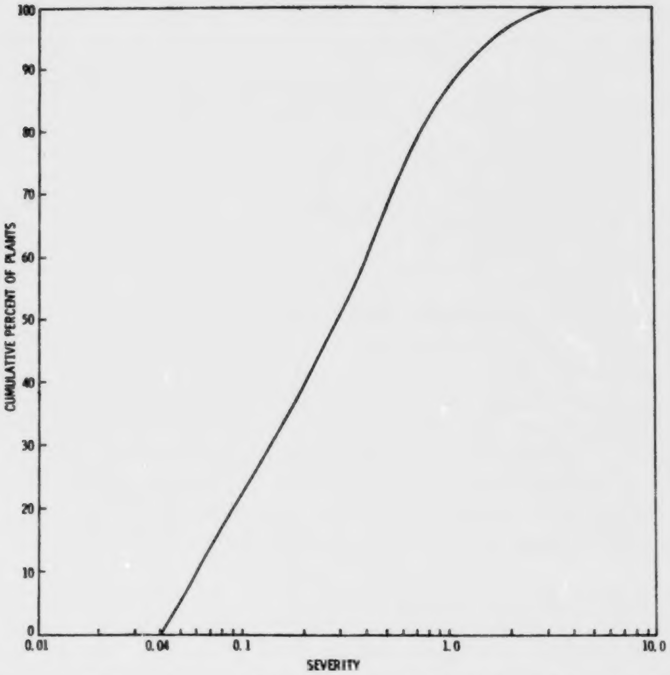


Figure 41. Severity distribution for total plant particulate emissions.

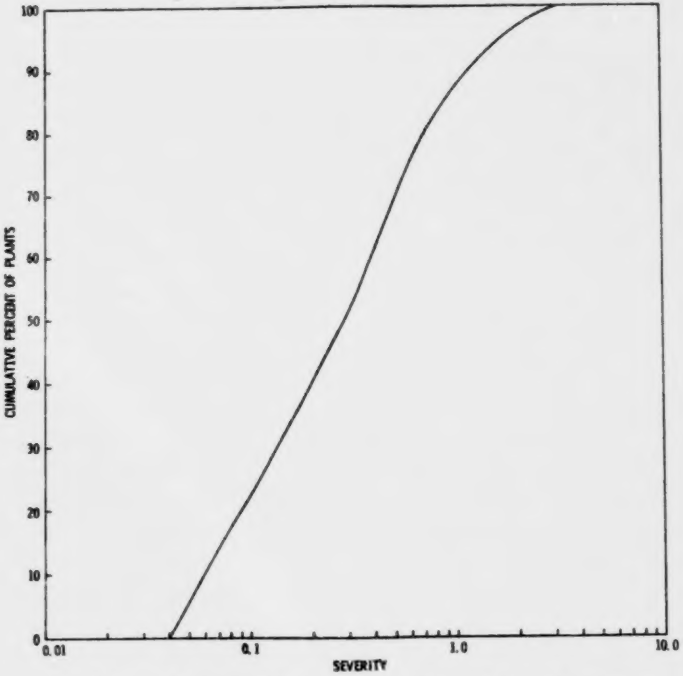


Figure 42. Severity distribution for total plant fluoride emissions.

TABLE 32. SEVERITY DISTRIBUTION SUMMARY

Emission point	Species	S Minimum	S Maximum	Percentage of plants S > 0.05	Percentage of plants S > 0.1
Total plant	Fluoride (as F)	0.04	2.9	90	10
	Particulate	0.04	2.9	90	10
	Ammonia	0.008	0.59	52	0

mass of each emission species emitted. A comparison with total particulate and SO_x emissions on a state-by-state and national basis can be made. Table D-1 in Appendix D shows the state emission burdens for the five criteria pollutants as reported in the National Emissions Data System (NEDS) (72). Table D-2 in Appendix D is an updated version of the NEDS data as computed by Monsanto Research Corporation under contract with EPA (73). Table D-2 was used for computations shown in Tables 33 through 39, which are presented and discussed later in this report.

a. Phosphoric Acid and Superphosphoric Acid Plants--
Total emissions from WPPA and superphosphoric acid manufacture are shown in Table 33. These were calculated by multiplying each emission factor at an emission point (Table 20) by the 1975 total annual production for the two chemicals: 6,291,000 metric tons for WPPA and 506,000 metric tons for superphosphoric acid.

The masses of emissions for criteria pollutants at WPPA (particulates and SO_x) and superphosphoric acid (particulaes) plants were calculated on a state-by-state basis for comparison with each state's total emissions burden. The resulting percentage of state burden for the industries and the contribution to the national burden are shown in Tables 34 and 35. The total mass of fluoride on a state-by-state basis is also included in the tables for completeness.

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(72) 1972 National Emissions Report; National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS). EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

(73) Eimutis, E. C., and R. P. Quill. State-by-State Listing of Source Types that Exceed the Third Decision Criterion, Special Project Report. Contract 68-02-1874, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 7, 1975. pp. 1-3.

TABLE 33. TOTAL ANNUAL MASS OF EMISSIONS FROM WET-PROCESS PHOSPHORIC ACID AND SUPERPHOSPHORIC ACID PLANTS (metric tons per year)

Emission point	Total fluoride	Particulate	SO_x
Wet process phosphoric acid:			
Rock unloading	0	912	0
Rock transport	0	281	0
Wet scrubber system	62	342	198
Gypsum pond	160 to 16,000	0	0
Superphosphoric acid:			
Wet scrubber	3.7	5.7 to 28	0

TABLE 34. WPPA INDUSTRY CONTRIBUTIONS TO STATE AND NATIONAL ATMOSPHERIC EMISSIONS

State	Number of plants	Total 1975 state production, 10^3 metric tons	Mass of emissions, metric tons/yr: Total fluoride[b]	Mass of emissions, metric tons/yr: Particulate	Mass of emissions, metric tons/yr: SO_x	Percent of state and national emissions[a]: Particulate	Percent of state and national emissions[a]: SO_x
Arkansas	1	35	1.2 to 84	8.4	1.1	0.006	0.0005
California	5	140	4.9 to 350	35	4.5	0.004	0.0002
Florida	13	3,384	122 to 8,400	855	108	0.4	0.006
Idaho	3	350	12 to 840	88	11.2	0.15	0.02
Illinois	4	260	9 to 660	66	8.3	0.006	0.0002
Iowa	1	155	5.4 to 390	40	5.0	0.02	0.001
Louisiana	4	1,060	37 to 2,700	260	34	0.07	0.015
Mississippi	1	142	4.8 to 345	35	4.5	0.02	0.002
North Carolina	1	470	17 to 1,140	118	15	0.02	0.0007
Texas	2	250	8.4 to 625	63	8.0	0.01	0.0004
Utah	1	45	1.6 to 114	11.5	1.4	0.02	0.0005
United States	36	6,291	222 to 16,000	1,540	200	0.01	0.0003

[a] Total state and national emissions data used in this calculation are given in Appendix C as obtained from References 72 and 73. State emission summary data were available only for criteria pollutants, not for fluoride.

[b] The range of fluoride emissions was based on wet scrubber emission factor (0.010 g/kg P_2O_5) plus gypsum pond emission factor range (0.025 to 2.5 g/kg P_2O_5).

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(30) 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

(31) Eimutis, E. C., and R. P. Quill. State-by-State Listing of Source Types that Exceed the Third Decision Criterion, Special Project Report. Contract 68-02-1874, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 7, 1975. pp. 1-3.

TABLE 35. SUPERPHOSPHORIC ACID INDUSTRY CONTRIBUTIONS TO STATE AND NATIONAL ATMOSPHERIC EMISSIONS

State	Number of plants	Total 1975 state production, 10^3 metric tons	Mass of emissions, metric tons/yr		Percent of state and national particulate emissions[b]
			Total fluoride[a]	Particulate	
Florida	3	220	1.6	12.1	0.005
Idaho	2	38	0.28	2.1	0.004
Louisiana	1	73	0.53	4.0	0.001
North Carolina	1	142	1.0	7.8	0.002
Texas	1	13	0.10	0.70	<0.001
Utah	1	20	0.15	1.1	0.001
United States	9	506	3.7	28	<0.001

[a] Based on upper limit emission factor of 0.055 g/kg P_2O_5.

[b] Total state and national emissions data used in this calculation are given in Appendix C as obtained from References 72 and 73. State emissions summary data were available only for criteria pollutants, not for fluoride.

b. Normal Superphosphate and Triple Superphosphate Plants--
The annual mass of emissions from all superphosphate plants in the United States is given in Table 36. A comparison with the total particulate and SO_x emissions in the United States in 1975 is included.

The mass of emissions from superphosphate plants on a state-by-state basis was also calculated, and resulting values were compared to each state's emissions burden. Tables 37, 38, and 39 show the results of this analysis.

c. Ammonium Phosphate Plants--
Mass emissions for each type of pollutant were found by multiplying average emission factors developed previously in this report by 1975 total production of 2.767 x 10^6 metric tons of P_2O_5. These values are approximately 4,150 metric tons of particulate, 105 metric tons of fluoride, and 190 metric tons of ammonia.

The mass of particulate emissions from ammonium phosphate plants on a state-by-state and national basis was compared to state and national emissions of particulates from all sources. State-by-state particulate emissions were estimated by apportioning national emissions according to the statewise plant capacity distribution in Appendix A. Table 40 shows the results of this comparison.

In 1975 an estimated 4,150 metric tons of particulates were emitted from ammonium phosphate manufacture, while in 1972 nationwide particulate emission loading from all sources was 17,872,000 metric tons (72). Thus, the ammonium phosphate industry

TABLE 36. ANNUAL MASS OF EMISSIONS FROM SUPERPHOSPHATE PLANTS IN THE UNITED STATES
(metric tons per year)

Emission source category	Mass of emissions		
	Fluoride	SO_x as SO_2	Particulate
NSP plants:			
Rock unloading			120
Rock feeders			24
Mixer and den	44		110
Curing building	830		1,600
Total plant	874		1,854
GTSP plants:			
Rock unloading			81
Rock feeders			15
Reactor, granulator, screens, cooler, dryer	110	1,700	45
Curing building	16	—	90
Total plant	126	1,700	231
ROP-TSP plants:			
Cone mixer, den, storage	60		96
Rock feeders			8
Rock unloading	—		42
Total plant	60		146
Total superphosphate industry	1,060	1,700	2,231

NOTE.—Blanks indicate species not emitted from this source category.

TABLE 37. CONTRIBUTION TO STATE PARTICULATE EMISSIONS BURDENS DUE TO EMISSIONS FROM NSP PLANTS

State	State production, metric tons/yr P_2O_5	Particulate emissions, metric tons/yr	Percent of state particulate burden
Alabama	29,600	124	0.00006
Arkansas	3,480	15	0.000009
Florida	44,700	188	0.00008
Georgia	66,800	280	0.0001
Illinois	58,700	246	0.00007
Indiana	8,130	34	0.00002
Kentucky	10,400	44	0.00002
Maryland	6,390	27	0.00004
Michigan	6,970	29	0.00001
Mississippi	3,480	15	0.00001
Missouri	8,710	37	0.00001
Nebraska	6,970	29	0.00001
New York	6,390	27	0.00001
North Carolina	43,000	180	0.00008
Ohio	6,390	27	0.000009
Pennsylvania	10,500	44	0.00001
South Carolina	25,600	107	0.00009
Tennessee	16,800	71	0.00004
Texas	22,600	95	0.00001
Utah	1,740	7	0.00003
Virginia	45,300	190	0.0001
Washington	6,390	27	0.00001
U.S. total	439,040	1,843	0.0014

TABLE 38. CONTRIBUTION TO STATE PARTICULATE EMISSIONS BURDENS DUE TO EMISSIONS FROM ROP-TSP PLANTS

State	State production, metric tons/yr P_2O_5	Particulate emissions, metric tons/yr	Percent of state particulate burden
Florida	477,200	116	0.00005
Idaho	17,730	4	0.000002
Missouri	26,240	6	0.000002
North Carolina	65,440	16	0.000007
Utah	10,500	3	0.000001
U.S. total	597,110	145	0.0001

TABLE 39. CONTRIBUTION TO STATE PARTICULATE AND SO_x EMISSIONS BURDENS DUE TO EMISSIONS FROM GTSP PLANTS

State	State production, metric tons/yr	Mass of emissions, metric tons/yr		Percent of state burden	
		Particulate	SO_x	Particulate	SO_x
Florida	706,200	181	1,313	0.00007	0.0007
Idaho	22,510	6	42	0.00002	0.0007
Mississippi	73,490	19	137	0.00001	0.0005
North Carolina	83,290	21	155	0.00001	0.00007
Utah	13,410	3	25	0.000001	0.00009
U.S. total	898,900	230	1,672	0.00018	0.003

TABLE 40. ESTIMATED MASS OF PARTICULATE EMISSIONS FROM AMMONIUM PHOSPHATE PLANTS

State	Percent of national production	Particulate emissions, metric tons: From ammonium phosphate plants	Particulate emissions, metric tons: From all sources (72)	Contribution to total emissions, %
Alabama	2	72	1,178,642	<0.1
Arizona	<1	9	72,684	<0.1
Arkansas	1	38	137,817	<0.1
California	2	99	1,006,452	<0.1
Florida	43	1,770	226,460	<0.1
Idaho	5	221	55,499	0.8
Illinois	2	96	1,143,027	0.4
Iowa	5	192	216,493	<0.1
Louisiana	24	988	380,551	0.1
Michigan	<1	21	705,921	0.3
Minnesota	1	53	266,730	<0.1
Mississippi	3	117	168,355	<0.1
Missouri	2	71	202,438	<0.1
North Carolina	2	78	481,026	0.1
Texas	6	247	549,408	<0.1
Utah	1	55	71,693	<0.1
Washington	<1	23	161,937	0.1
U.S. total	100	4,150	17,872,000	<0.1

contributed approximately 0.02% of total national particulate emissions. Similar information on a statewise basis is presented in Table 40. In no state do ammonium phosphate particulate emissions represent over 1% of statewide particulate emissions, while particulate emissions from ammonium phosphate production are responsible for more than 0.1% of total statewide particulate emissions in only 3 of the 17 producing states.

3. Affected Population

The number of persons living in the area around a plant who are exposed to a contaminant concentration exceeding a given level is denoted as the affected population. Plume dispersion equations are used to determine the area where the average ground level concentration, $\overline{\chi}$, exceeds a given value. In the source assessment program two reference values are used, $\overline{\chi}/F = 1.0$ and $\overline{\chi}/F = 0.05$. This area, so determined, is then multiplied by an average population density to determine the affected population.

Disperson equations predict that $\overline{\chi}$ varies with the distance, X, downwind from a source. For elevated sources, $\overline{\chi}$ is zero at the source (where X equals 0), increases to some maximum value, $\overline{\chi}_{max}$, as X increases and then falls back to zero as X approaches infinity. Therefore, a plot of $\overline{\chi}$ versus X will have the appearance illustrated in Figure 43.

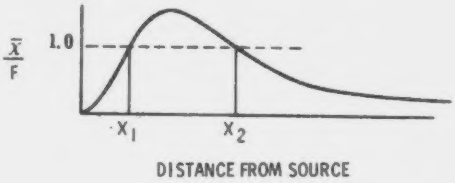

Figure 43. $\overline{\chi}/F$ as a function of distance from an elevated source.

For fugitive emissions where the stack height is zero, the value of $\overline{\chi}/F$ is a maximum at the source and decreases with distance downwind according to Figure 44.

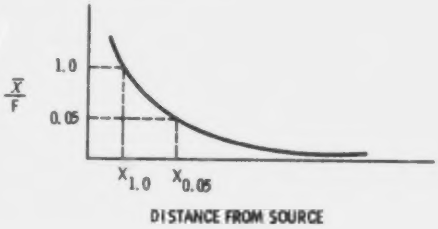

Figure 44. General distribution of $\overline{\chi}/F$ as a function of distance for a ground level source.

The value for the population density around a representative plant is determined by averaging county population densities in which actual plants are located. However, because the population patterns within a given county may vary significantly, the actual population density in the immediate vicinity of individual plants may be lower than this average. Conclusions, therefore, should not be drawn with regard to actual environmental impacts at individual plant sites.

Due to uncertainties inherent in sampling and dispersion modeling methodologies, the number of persons around a representative plant exposed to a $\overline{\chi}/F$ ratio greater than 0.05 is reported in addition to $\overline{\chi}/F > 1.0$. The mathematical derivation of the affected population calculation is presented in Reference 69.

a. Phosphoric and Superphosphoric Acid Plants--
The county population density around average WPPA and superphosphoric acid plants is 46.1 persons/km^2. The affected population values for those emission species and sources where the ratio of $\overline{\chi}$ to F exceeds 0.05 and 1.0 are given in Table 41. Affected population values for SO_x were zero and are not shown in the table.

TABLE 41. AFFECTED POPULATION VALUES FOR EMISSIONS FROM WET PROCESS PHOSPHORIC ACID AND SUPERPHOSPHORIC ACID PLANTS

Emission source	Affected population, persons			
	Fluoride		Particulates	
	$\bar{\chi}/F>0.05$	$\bar{\chi}/F>1.0$	$\bar{\chi}/F>0.05$	$\bar{\chi}/F>1.0$
Wet process phosphoric acid:				
Rock unloading	0	0	64	0
Rock transfer and charging	0	0	2	0
Wet scrubber	159	0	0	0
Gypsum pond	5,532	0	0	0
Superphosphoric acid:				
Wet scrubber	28	0	0	0

In calculating affected population values for fluoride emissions from a typical gypsum pond, it was assumed that no one lived within 2,000 m of the edge of the pond, or 2,600 m of the center of the pond. The value of $\bar{\chi}/F$ drops below 1.0 at 1,300 m from the center of the pond, resulting in no affected population. The value of $\bar{\chi}/F$ drops below 0.05 at 6,700 m from the center of the pond, resulting in an affected population value of 5,532 persons.

b. Normal Superphosphate and Triple Superphosphate--

Affected population values for emissions from average superphosphate plants are shown in Table 42 for those emission points with at least one pollutant which has source severity greater than or equal to 0.05. For those emissions with source severity less than 0.05, there is no population affected by a ground level concentration for which $\bar{\chi}/F$ is greater than or equal to 0.05.

TABLE 42. AFFECTED POPULATION VALUES FROM SUPERPHOSPHATE PLANTS

Emission source	Affected population, persons					
	$\bar{\chi}/F>0.05$			$\bar{\chi}/F>1.0$		
	Particulate	Fluoride	SO_x	Particulate	Fluoride	SO_x
NSP:						
Mixer and den	0	529		0	0	
Curing building	519	13,021		0	539	
ROP-TSP:						
Cone mixer, den, curing building	0	1,178		0	0	
Rock unloading	5			0		
GTSP:						
Reactor, granulator, dryer, cooler, screens	0	1,356	307	0	0	0
Curing building	0	161		0	0	
Rock unloading	15			0		

NOTE.—Blanks indicate no emission of the species for the source.

c. Ammonium Phosphate Plants--
Results of affected population calculations for the average source are presented in Table 43. The average population density was 82 persons/km².

TABLE 43. AFFECTED POPULATION VALUES FROM AMMONIUM PHOSPHATE PLANTS

	Affected population, persons					
	Fluoride		Particulate		Ammonia	
Emission source	$\bar{\chi}/F>0.05$	$\bar{\chi}/F>1.0$	$\bar{\chi}/F>0.05$	$\bar{\chi}/F>1.0$	$\bar{\chi}/F>0.05$	$\bar{\chi}/F>1.0$
Total plant stack emission	285	0	288	0	41	0

G. AIR POLLUTION CONTROL TECHNOLOGY

1. Phosphoric Acid and Superphosphoric Acid

Environmental and economic concerns have prompted use of control devices in most facets of the WPPA and superphosphoric acid industry, with the exception of volatile emissions from the gypsum pond. The problem of pollutant abatement in the industry is generally approached by using add-on devices. Process modifications are not employed because of the delicate balance of operating conditions required to produce filterable gypsum crystals. Process technology has been developed to recover fluoride and gypsum byproducts, offering a more economically attractive way for the WPPA industry to reduce wastes.

The following sections discuss various controls and byproduct recovery processes currently in use to reduce air pollutant levels.

a. Dust Control in Raw Materials Handling Operations--
Enclosed operation and baghouses are typical methods of control at ground phosphate rock unloading stations. Satisfactory control of dust emissions from unloading hopper-bottom railroad cars or trucks is achieved by baghouses which realize high efficiency in collection of this size particle (60% to 80% of the rock is less than 74 μm (24). Efficiencies are reported to be greater than 99% (74).

Feed hoppers, storage bins, and conveyors are also enclosed to reduce particulate emissions and moisture contamination of the rock. When transport of ground rock from storage bin to feed hopper is accomplished by pneumatic conveyors, a cyclone separator and baghouse are located at the destination for control of bulk material and discharged dust.

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(74) Seinfeld, J. H. Air Pollution: Physical and Chemical Fundamentals. McCraw-Hill Book Co., New York, New York, 1975. 523 pp.

Future rock grinding operations may utilize a wet grinding circuit rather than the current dry grinding practice. Wet grinding, because it also means wet rock receipt and storage, leads to a reduction in particulate emissions as well as energy savings by eliminating a rock drying step.

b. WPPA Wet Scrubber Systems--

Of the available types of pollution control, wet scrubbers have been the exclusive choice for treatment of contaminated process vapors generated in the digester, filter, and evaporator. These scrubbers combine the ability to absorb gaseous fluorides and remove particulates by impaction on the liquid droplets. Problems in scrubber efficiency result from deposition of hydrated silica within water nozzles or scrubber packing, which affects liquid-vapor contact.

Crossflow packed scrubbers provided high absorption capabilities and tend to operate free from plugging when preceded by a spray section (28). When gases enter the spray section, hot vapors are cooled, high concentrations of fluorides and particulates are reduced, and reaction takes place between the water and silicon tetrafluoride in the gas.

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2 \qquad (30)$$

The silica (SiO_2) precipitates in the form of a hydrated gel [$Si(OH)_4$].

$$SiO_2 + 2H_2O \longrightarrow Si(OH)_4 \qquad (31)$$

When fluoride and particulate loading is substantially reduced, gas passes through the more efficient stage, a cross-flow packed scrubber, where the remaining hydrogen fluoride and particulates are removed (28). The crossflow design, with scrubbing spray normal to the direction of the gas flow, washes precipitates off the packing to prevent plugging. The collected deposits are near the front of the packed bed, which is more heavily irrigated to reduce solids buildup (75). Overall efficiencies for a spray-crossflow packed scrubber have been reported to be greater than 99% (31). A diagram of this scrubber design is presented in Figure 45.(31).

Although venturi scrubbers provide effective contact and gas absorption, they have a major disadvantage in that a high pressure drop (2.5 kPa to 12.4 kPa) and corresponding high energy requirement are necessary to meet the given standards for emissions (15). A venturi may be used instead of a spray tower upstream from the packed scrubber described in the previous paragraph, or in conjunction with a cyclonic spray tower.

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(75) Environmental Engineers' Handbook, Volume 2, Air Pollution, B. G. Liptak, ed. Chilton Book Co., Radnor, Pennsylvania. 1974. 1340 pp.

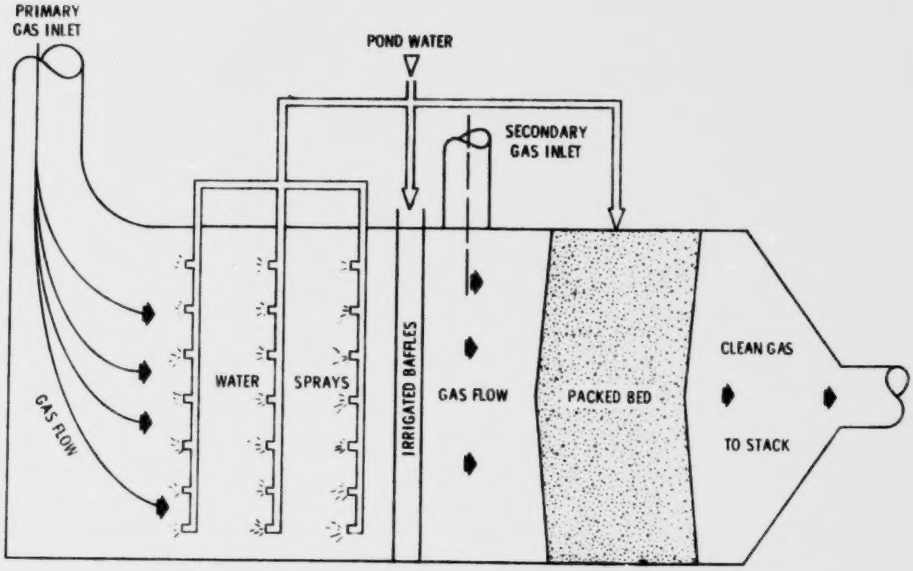

Figure 45. Spray-crossflow packed scrubber (31).

Important factors observed in efficiencies of control devices are composition and temperature of scrubbing water. Gypsum pond water contains 3,000 ppm to 10,000 ppm fluorine. The partial pressure of the hydrogen fluoride in the pond water makes efficient recovery of fluorides in the contaminated gas stream difficult (17, 64). The mass transfer process may even become inoperative at higher temperatures. To combat this effect, some industries use fresh water in the last stage of the scrubber to reduce gaseous fluorides to an acceptable level.

The temperature influence on scrubber outlet concentrations is depicted in Figure 46 (76).

c. Superphosphoric Acid Wet Scrubber--
As in WPPA plants, superphosphoric acid plants treat exhaust air with wet scrubbers to remove particulates and gaseous fluorine compounds. The type of wet scrubber used in this application, however, is different from the WPPA choice because of a lower gas flow rate. A water-induced venturi scrubber, shown in Figure 47, is the typical choice (31).

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(76) Specht, R. C., and R. R. Calaceto. Gaseous Fluoride Emissions from Stationary Sources. Chemical Engineering Progress, 63(5):7884, 1967.

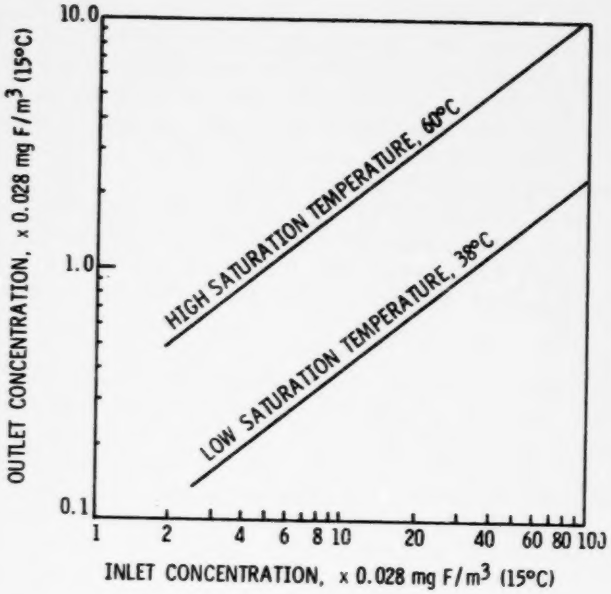

Figure 46. Inlet concentration versus outlet concentration at scrubber discharge temperatures for a cyclonic spray tower (76).

Reprinted from Chemical Engineering Progress by courtesy of the American Insititute of Chemical Engineers.

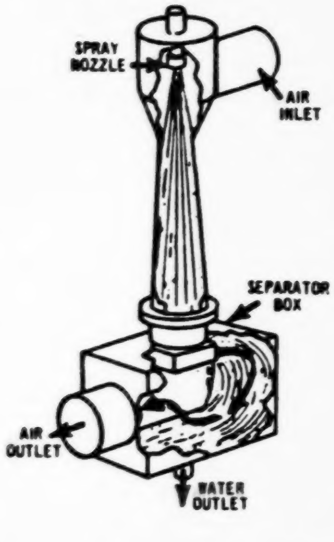
SPRAY NOZZLE
AIR INLET
SEPARATOR BOX
AIR OUTLET
WATER OUTLET

Figure 47. Water-induced venturi scrubber (31).

The gas stream to the scrubber is from a combination of sources: barometric condenser, hot well vents, and product cooler tank. The enclosed system is maintained at a slight negative pressure to induce inward leakage at openings in access ways and equipment, thus eliminating potential fugitive emissions. Scrubbers installed to handle the exhaust streams are of nominal capacity, about 4.2 m^3/s, regardless of plant size (77). Because of the low gas flow rate and availability of large amounts of gypsum pond water, scrubbing requirements for superphosphoric acid plants can be met with the venturi ejector without use of mechanically more complicated packed and conventional venturi scrubbers (31).

The water-induced venturi does not depend on gas flow for motive power. The ejector venturi uses a large liquid spray under high pressure to induce air flow through the throat section, where intimate gas-liquid contact occurs. This unit is followed by a gas-liquid separation chamber to prevent entrainment of the contaminated liquid droplets in the exhausted gas. Efficient separation is achieved by a cyclonic section, which also removes remaining particulates. An alternative is a packed or cyclonic-packed scrubber in the separator vessel.

Scrubber efficiency is increased with higher liquid-to-gas ratios and with increasing nozzle pressure. Plant data indicate that these installations are 99% to 99.8% efficient (31).

2. Normal Superphosphate and Triple Superphosphate

Superphosphate production and storage facilities utilize a variety of devices including wet scrubbers, cyclones, and baghouses to control emissions of particulates, fluorides, and combustion gases (31, 32).

Particulate emissions from ground rock unloading, storage, and transfer systems are controlled by baghouse collectors. Cloth filters have reported efficiencies of over 99.9% for particles smaller than 75-μm (Appendix B). Collected solids are recycled to the process.

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(77) Frazier, A. W., E. F. Dillard, and J. R. Lehr. Chemical Behavior of Fluorine in the Production of Wet Process Phosphoric Acid. Presented at the American Chemical Society Annual Meeting, Chicago, Illinois, August 24-29, 1975. 16 pp.

Emissions of silicon tetrafluoride, hydrogen fluoride, and particulate from the production area and curing buildings are controlled by scrubbing the offgases with recycled water. Wet scrubbing combines the ability to remove particulate by impaction on the surface of liquid droplets with the ability to absorb gaseous fluoride compounds into the liquid phase. Exhausts from the dryer, cooler, screens, mills, and curing building, where heavier loadings of particulate may be present, are sent first to a cyclone separator and then to a wet scrubber.

Gaseous silicon tetrafluoride in the presence of moisture reacts as follows:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6 \qquad (32)$$

The silica is present as a gelatinous mass of polymeric silica which has the tendency to plug scrubber packings. The use of conventional packed countercurrent scrubbers and other contacting devices with small gas passages for controlling silica is therefore limited. Scrubber types that can be used within this restriction are 1) spray tower, 2) cyclonic scrubbers, 3) venturi scrubbers, 4) impingement type scrubbers, 5) jet ejector scrubbers, and 6) spray-crossflow packed scrubbers.

Spray towers are not capable of the high efficiencies (greater than 95%) required for compliance with present regulations. They find use, however, as precontactors for fluorine removal at relatively high concentration levels (greater than 3,000 ppm).

Air pollution control techniques vary from plant to plant depending on particular plant designs. The effectiveness of abatement systems for the removal of fluoride and particulate varies from plant to plant depending on a number of factors. The effectiveness of fluorine abatement is determined by 1) inlet fluorine concentration, 2) outlet or saturated gas temperature, 3) composition and temperature of the scrubbing liquid, 4) scrubber type and transfer units, and 5) effectiveness of entrainment separation (16, 31). Control effectiveness is enhanced by increasing the number of scrubbing stages in series and by using fresh water scrub in the final stage. Reported efficiencies for fluoride control range from less than 90% to over 99% depending on inlet fluoride concentrations and the system employed. An efficiency of 98% for particulate control is achievable (31).

3. Ammonium Phosphate

Emission control technology applied to DAP production serves three purposes: recovery of ammonia, recovery of particulate MAP and DAP, and prevention of pollutant emissions of ammonia, fluorides, and particulates. Common practice in the industry is to combine emission points for emission control: reactor and ammoniator-granulator, dryer and cooler, and product sizing and material transfer. Reactor and ammoniator-granulator emissions are vented directly to a wet scrubber system, while emissions from remaining sources pass through cyclone collectors for product recovery and recycle before passing to a wet scrubber system.

The chemistry for ammonia recovery is identical to the process chemistry discussed earlier: Ammonia is scrubbed from offgases with excess phosphoric acid where it reacts to form ammonium phosphates which are retained in the scrubbing liquor. Silicon tetrafluoride, the primary gaseous fluoride emission species, is scrubbed from offgases according to reactions in Equations 33 and 34.

$$2HF + SiF_4 \rightleftarrows H_2SiF_6 \tag{33}$$

$$3SiF_4 + 4H_2O \rightleftarrows Si(OH)_4 + 2H_2SiF_6 \tag{34}$$

All ammoniation-granulation plants have some form of pollution control equipment, but a complete characterization of emission control practices of the industry is not available (5). Combined requirements for particulate collection and gas absorption for ammonia recovery and fluoride emission control permit application of a wide variety of scrubber types for DAP service. Devices applied to DAP emission control include

- Spray towers
- Venturi scrubbers
- Impingement scrubbers
- Spray-crossflow packed bed scrubbers

Spray towers provide the interphase contacting necessary for gas absorption by dispersing scrubbing liquid in the gas phase as a fine spray. Several types of spray towers are in general use. The simplest consists of an empty tower equipped with liquid spray nozzles at the top and a gas inlet at the bottom. Scrubbing liquor sprayed into the gas stream falls by gravity through the upward flowing contaminated gas. A disadvantage of this device is entrainment of scrubbing liquid aerosols into the exit gas stream.

Cyclonic spray towers eliminate excessive droplet entrainment by using centrifugal force to remove droplets. Figure 48 presents schematic diagrams of one- and two-stage cyclonic spray tower scrubbers. Gas enters the scrubber tangentially and scrubber liquor is directed parallel to gas flow, providing crossflow contacting of gas and liquid streams (11, 43).

Venturi scrubbers (Figure 49) are particularly well suited for streams with high solids or silicon tetrafluoride loadings because of their high solids handling capacity and self-cleaning characteristics. A venturi provides a high degree of gas-liquid mixing, but relatively short contact time and cocurrent flow

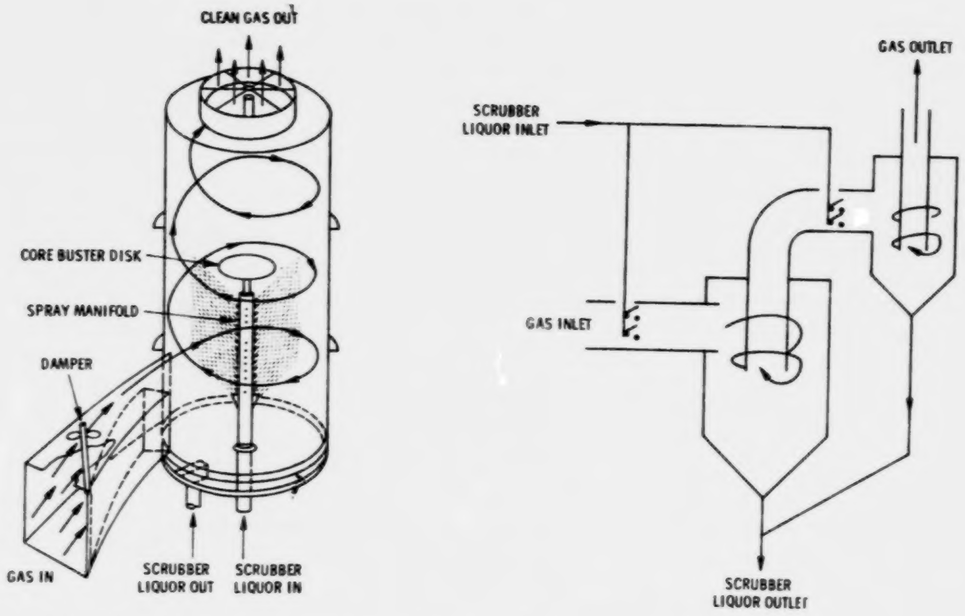
CLEAN GAS OUT
CORE BUSTER DISK
SPRAY MANIFOLD
DAMPER
GAS IN
SCRUBBER LIQUOR OUT
SCRUBBER LIQUOR IN
GAS OUTLET
SCRUBBER LIQUOR INLET
GAS INLET
SCRUBBER LIQUOR OUTLET

Figure 48. Cyclonic spray tower scrubbers (11, 45).

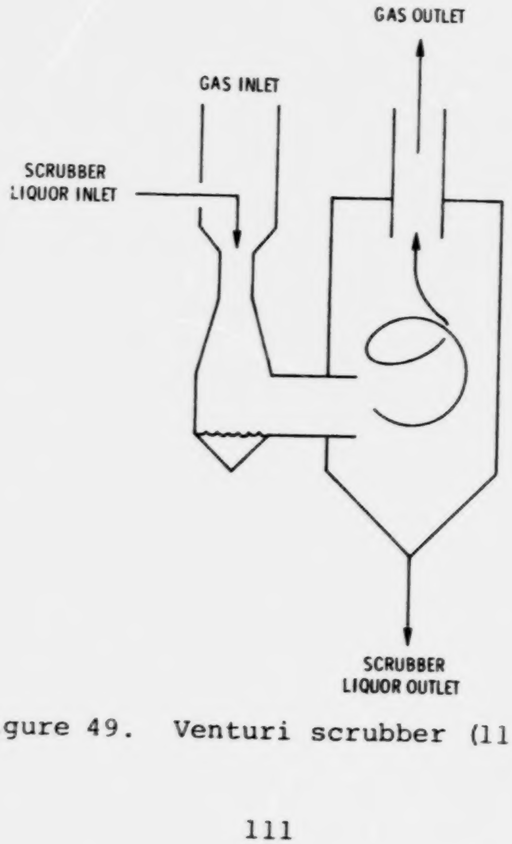
GAS OUTLET
GAS INLET
SCRUBBER LIQUOR INLET
SCRUBBER LIQUOR OUTLET

Figure 49. Venturi scrubber (11).

limit absorption capabilities. Scrubbing liquor is introduced at high velocity through a nozzle upstream of the venturi throat, and water velocity pulls flue gas through the venturi. Entrained scrubbing liquor requires a mist eliminator. The cyclone in Figure 49 is used to remove mists. In application to DAP emissions, venturi scrubbers are often used as the initial component of a multiple scrubber system (11).

Although impingement scrubbers are primarily particulate collection devices, they also possess some absorption capability. The Doyle scrubber pictured in Figure 50 is most commonly used by the fertilizer industry.

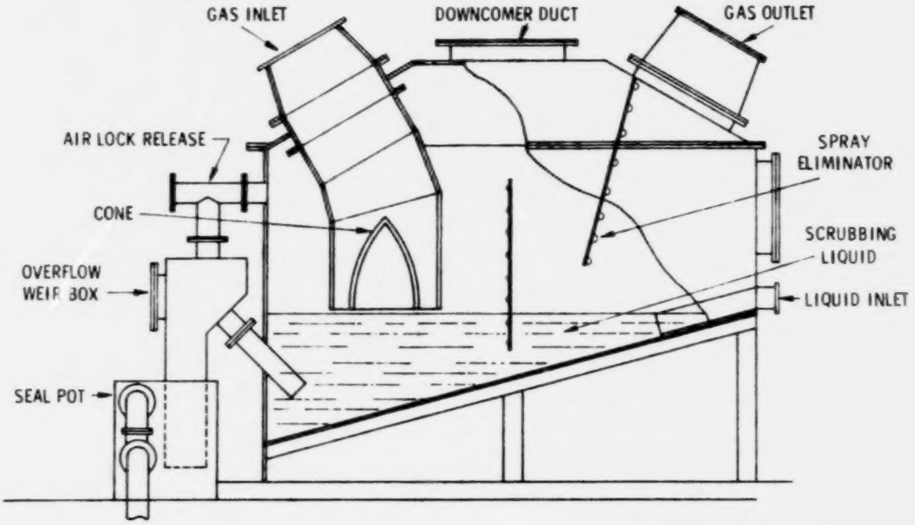

Figure 50. Doyle impingement scrubber (11).

Effluent gases are introduced into the scrubber as shown in Figure 50. The lower section of the inlet duct is equipped with an axially located core that causes an increase in gas stream velocity prior to its impingement on the scrubbing liquor surface. Effluent gases contact the pool of scrubbing liquid at a high velocity and undergo a reversal in direction. Solids impinge on the liquid surface and are retained, while absorption of gaseous fluorides is promoted by interphase mixing generated by impact. Solids handling capacity is high; however, absorption capability is very limited (11).

The spray-crossflow packed bed scrubber shown earlier in Figure 45 consists of two sections--a spray chamber and a packed bed--separated by a series of irrigated baffles. Both spray and packed sections are equippped with a gas inlet. Effluent streams with relatively high fluoride concentrations--particularly those rich in silicon tetrafluoride--are treated in the spray chamber before entering the packing. This preliminary scrubbing removes silicon tetrafluoride, thereby minimizing bed plugging. It also reduces packed stage loading and provides some solids handling capacity. Gases low in silicon tetrafluoride can be introduced directly to the packed section.

The spray section consists of a series of countercurrent spray manifolds with each pair of spray manifolds followed by a system of irrigated baffles. Irrigated baffles remove precipitated silica and prevent formation of scale in the spray chamber.

Packed beds of both cocurrent and crossflow design have been tried; crossflow design has proven to be more dependable. Crossflow design operates with the gas stream moving horizontally through the bed while scrubbing liquid flows vertically through the packing. Solids tend to deposit near the front of the bed where they can be washed off by a cleaning spray. The back portion of the bed is usually operated dry to provide mist elimination.

Spray-crossflow packed bed scrubbing is effective from a gas absorption standpoint, but it is less effective for collecting particulate; hence, it is used as a "tail gas" or secondary scrubber following a particulate scrubber. Packed scrubbers are seldom used as primary scrubbers due to their tendency to plug with gelatinous silicon or DAP (45).

Equipment commonly used for primary scrubbing includes venturis and cyclonic spray towers, while cyclonic spray towers, impingement scrubbers, and spray-crossflow packed bed scrubbers are used as secondary scrubbers (11, 43, 45). Primary scrubbers generally use 20% to 30% P_2O_5 phosphoric acid as scrubbing liquor principally to recover ammonia (45). Secondary scrubbers generally use gypsum pond water principally for fluoride control.

Throughout the industry, however, there are many combinations and variations. Some plants use reactor-feed concentration phosphoric acid (40% P_2O_5) in both primary and secondary scrubbers, and some use phosphoric acid near the dilute end of the 20% to 30% P_2O_5 range in only a single scrubber (31, 43). Existing plants are equipped with ammonia recovery scrubbers on the reactor, ammoniator-granulator, and dryer, and particulate controls on the dryer and cooler. Additional scrubbers for fluoride removal are common but not typical. Only 15% to 20% of installations contacted in an EPA survey were equipped with spray-crossflow packed bed scrubbers or their equivalent for fluoride removal (11).

Emission control efficiencies for DAP plant control equipment have been reported as:

Ammonia	94% to 99% (11, 45)
Particulates	75% to 99.8% (45, 71)
Fluorides	74% to 94% (11)

Fluoride emissions and the need for controlling them could be eliminated from DAP production if fluorides were removed from phosphoric acid raw material. As shown earlier in Table 16, furnace phosphoric acid has very little (less than 1 ppm) fluorine content, but essentially all ammonium phosphates are currently produced from WPPA. Furnace acid is not used primarily because it costs 29% more per metric ton of P_2O_5 to produce than WPPA (78).

Particulate collection efficiency of dry cyclones increases as gas flow rate increases. However, increasing exhaust gas flow rate also increases gas flow rate through the dryer. It has been reported that additional dust is emitted from the discharge end of the dryer when gas velocity exceeds 112 m/min (46). One way to increase gas velocity in the cyclone, but not in the dryer, is to install an open duct in the exhaust line between the cyclone and dryer and cooler discharge as shown in Figure 51. Gas velocity through the dryer and cooler can then be regulated by means of the damper.

H. BYPRODUCT RECOVERY

Fluorine compounds volatilized during production of phosphate fertilizer materials are being considered as a valuable resource for production of fluosilicates, fluorides, and hydrofluoric acid (63). Fluorine is recovered from gas effluent streams as a weak solution of fluosilicic acid by the following reaction sequence:

$$\text{Phosphate rock} + \text{acid} \longrightarrow HF \qquad (35)$$

$$4HF + SiO_2 \longrightarrow SiF_4 + H_2O \qquad (36)$$

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2 \qquad (37)$$

Calcium fluoride contained in the rock reacts with acid to form hydrogen fluoride. This hydrogen fluoride in turn reacts with silica present in the rock to form silicon tetrafluoride. Silicon tetrafluoride vapor dissolves readily in an aqueous scrubbing solution to form fluosilicic acid. Silica formed during absorption of silicon tetrafluoride is removed by filtration and the product is a solution of 17% to 25% fluosilicic acid (63). Systems recover the acid at concentrations of 25% or less, a constraint which results from a rapid increase in vapor pressure

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(78) Environmental Considerations of Selected Energy Conserving Manufacturing Process Options, Vol. 13, Phosphorus/Phosphoric Acid Industry Report. EPA-600/7-76-034m (PB 264 279), U.S. Environmental Protection Agency, Cincinnati, Ohio, December 1976. 96 pp.

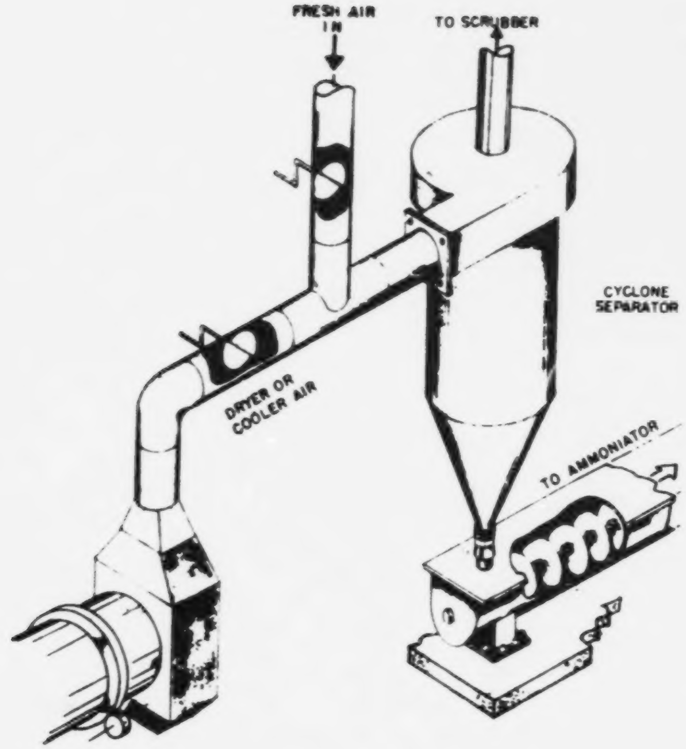

Figure 51. Cyclone gas velocity control (46).

at higher concentrations. The small amount of silica-containing liquid waste generated is normally consumed as a filler in fertilizer production.

A number of plants in the phosphate fertilizer industry are currently practicing recovery techniques. Approximately 60% of NSP plants recover fluorine as a weak solution of fluosilicic acid utilizing two-or three-stage wet scrubbing systems.

Between 10% and 20% of WPPA plants recover fluorine during evaporation-concentration of the phosphoric acid. Two systems available for fluosilicic acid recovery are inventions of the Swenson Evaporation Co. and Swift & Co. (22, 27). The Swenson system involves condensation of evaporator vapors and flash evaporation to produce an approximately 15% solution. In the Swift process, a weak solution of fluosilicic acid scrubs the fluoride-containing vapors from the evaporator and flows to a recirculation tank. Fluosilicic acid (about 18% to 20%) is bled from the tank, and water is added to the recycled solution to maintain the required concentration of acid for scrubbing.

An alternative method of fluorine recovery is removal of fluosilicate salts prior to concentration of the approximately 30% P_2O_5 acid. One procedure involves addition of sodium carbonate to the filtered solution of weak acid and subsequent precipitation of sodium fluosilicate.

Process modifications to recover fluoride byproducts reduce emissions from the WPPA scrubber and gypsum ponds by removing fluoride from process streams. The emission factor developed for the scrubber system at WPPA plants recovering fluoride byproducts was one-half the factor for plants not practicing recovery techniques.

SECTION 5

WATER EFFLUENTS

Because of the integrated nature of the phosphate fertilizer industry, considering the wastewater handling practices of the industry as a whole is necessary. Wastewater arising from different manufacturing operations are often combined for treatment at one location. The integrated character of the industry can be seen in Table 44. Over 70% of the plants produce only one type of phosphate fertilizer material, while 30% of all the plants consist of multiunit operations. However, more than 80% of phosphate fertilizer production occurs at multiunit plants.

TABLE 44. DESCRIPTION OF PHOSPHATE FERTILIZER COMPLEXES IN THE UNITED STATES BY UNIT OPERATIONS

Unit operations at plant site	Number of plants	Percent of total
WPPA	5	4.1
NSP	61	50.4
DAP	23	19.0
WPPA, SPA	3	2.5
WPPA, NSP	1	0.8
WPPA, TSP	2	1.7
WPPA, DAP	10	8.3
WPPA, TSP, DAP	6	5.0
WPPA, SPA, DAP	2	1.7
WPPA, NSP, TSP	1	0.8
NSP, TSP, DAP	1	0.8
WPPA, SPA, TSP, DAP	4	3.3
WPPA, NSP, TSP, DAP	2	1.7
Total	121	100

WPPA--wet process phosphoric acid.
SPA--superphosphoric acid.
NSP--normal superphosphate.
TSP--triple superphosphate (includes both granular and run-of-pile).
DAP--diammonium phosphate (some plants also make monoammonium phosphate).

The remainder of this section considers wasewater handling practices, gypsum pond characteristics, effects of lime treatment, and potential environmental effects of those plants that do discharge wastewaters.

A. SOURCES OF WASTEWATER

Two basic wastewater source types exist in a phosphate fertilizer plant--point and nonpoint. Point sources are those which originate as a definite wastewater stream from a particular process. Nonpoint sources originate from random leaks or from large areas within a plant. Point sources for each of the five basic processes are discussed first, below, followed by a general discussion of nonpoint sources for the entire plant.

1. Point Sources

Point sources of wastewater generated at phosphate fertilizer plants can be divided into three general classes:

- Contact process water
- Noncontact cooling water
- Steam condensate

Contact process wastewater refers to any water which, during manufacturing or processing, comes into direct contact with or results from production or use of any material, intermediate product, finished product, byproduct, or waste product.

a. Phosphoric Acid--

Sources of contact process wastewater from WPPA production include wet scrubber liquor, gypsum slurry water, and barometric condensers (Figure 52). Recycled gypsum pond water is used in the wet scrubber system to remove particulates, fluorides, and phosphates from the gas streams. This reservoir of contaminated process water also supplies the water requirements for transferring waste gypsum to a disposal area and for operation of barometric condensers. Acid sludge underflow, generated in acid clarification, contains substantial amounts of phosphate and is normally disposed of by blending into a dry fertilizer (usually TSP); it does not enter the pond system.

Once-through or recirculated noncontact cooling water is used to control the exothermic reaction when concentrated sulfuric acid is diluted. Cooling water may be either recirculated gypsum pond water or a separate nonprocess stream that is recycled or discharged. Significant quantities of steam are used in WPPA production. In many plants, the steam is used on a once-through basis. Uncontaminated steam condensate is discharged to the receiving waters without treatment. Contaminated steam condensate, such as that from barometric condensers and vacuum ejectors, is discharged to the gypsum pond.

Wastewater streams at phosphoric acid plants are contaminated to varying degrees by quantities of phosphoric acid, fluorides, sulfates, and gypsum.

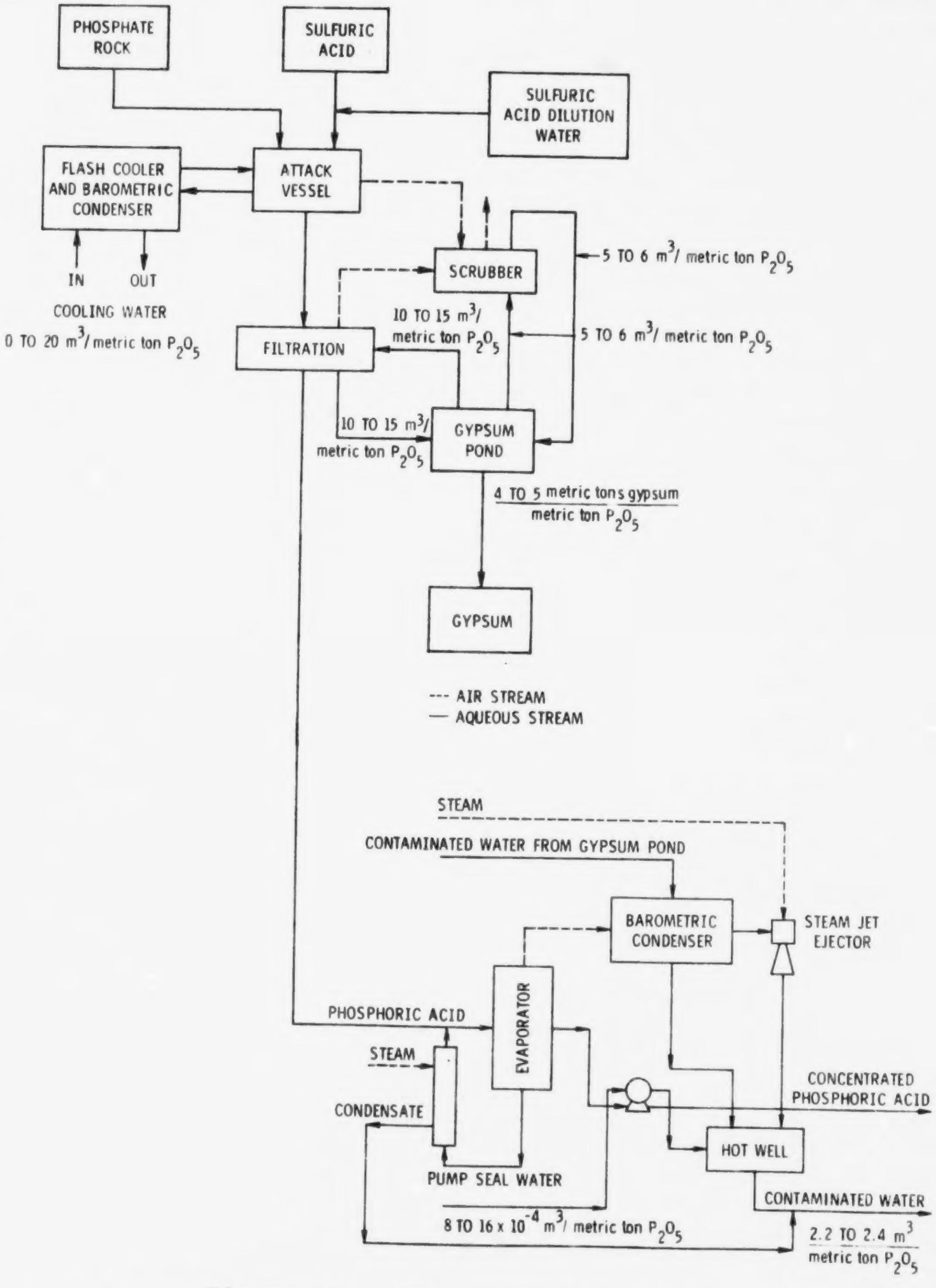
PHOSPHATE ROCK
SULFURIC ACID
SULFURIC ACID DILUTION WATER
FLASH COOLER AND BAROMETRIC CONDENSER
ATTACK VESSEL
IN
OUT
COOLING WATER
0 TO 20 m^3/ metric ton P_2O_5
SCRUBBER
5 TO 6 m^3/ metric ton P_2O_5
FILTRATION
10 TO 15 m^3/ metric ton P_2O_5
5 TO 6 m^3/ metric ton P_2O_5
10 TO 15 m^3/ metric ton P_2O_5
GYPSUM POND
4 TO 5 metric tons gypsum / metric ton P_2O_5
GYPSUM
--- AIR STREAM
— AQUEOUS STREAM
STEAM
CONTAMINATED WATER FROM GYPSUM POND
BAROMETRIC CONDENSER
STEAM JET EJECTOR
EVAPORATOR
PHOSPHORIC ACID
STEAM
CONDENSATE
CONCENTRATED PHOSPHORIC ACID
HOT WELL
PUMP SEAL WATER
CONTAMINATED WATER
8 TO 16 x 10^{-4} m^3/ metric ton P_2O_5
2.2 TO 2.4 m^3 / metric ton P_2O_5

Figure 52. WPPA production (17).

b. Superphosphoric Acid--

Superphosphoric acid plants are located at fertilizer complexes producing WPPA. As a result, water usage requirements are supplied for the most part by the existing water recycle system. Process wastewater streams at superphosphoric acid plants come from the barometric condensers, steam jet ejectors, and wet scrubbers. These streams pick up quantities of phosphoric acid and fluorides and are returned to the gypsum pond for reuse at the phosphate fertilizer complex. Noncontaminated steam condensate may be segregated into a separate nonprocess water system and recycled or discharged.

c. Normal Superphosphate

The only process wastewater stream generated at NSP plants is the wet scrubber liquor used to reduce the level of fluoride gases and particulate matter evolved from the mixer, den, and conveyors (Figure 53). Scrubber liquor is discharged to a water containment or pond system and reused. Nearly two-thirds of the NSP plants presently practice fluorine recovery, thereby eliminating or greatly reducing the need for a pond. In this system, fluorine in the exhaust gas stream is recovered as a weak solution of fluosilicic acid. NSP plants recoverying fluosilicic acid consume the small amount of silica-containing liquid waste generated as a filler in fertilizer production and report no discharge of wastewater.

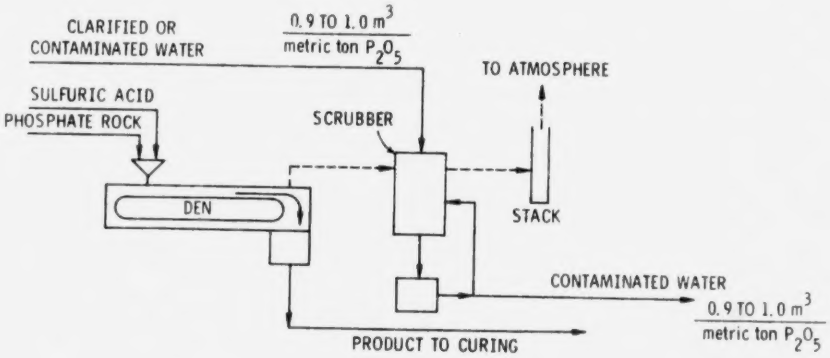
CLARIFIED OR
CONTAMINATED WATER
$\frac{0.9 \text{ TO } 1.0 \text{ m}^3}{\text{metric ton } P_2O_5}$
TO ATMOSPHERE
SULFURIC ACID
PHOSPHATE ROCK
SCRUBBER
DEN
STACK
CONTAMINATED WATER
$\frac{0.9 \text{ TO } 1.0 \text{ m}^3}{\text{metric ton } P_2O_5}$
PRODUCT TO CURING

Figure 53. NSP production (17).

d. Triple Superphosphate

The wet scrubber liquor is the only process wastewater stream generated at TSP production units (Figures 54 and 55). Recycled gypsum pond water is used in the scrubber system to reduce the level of fluoride gases and particulate matter evolved during fertilizer production and storage.

e. Ammonium Phosphate--

At ammonium phosphate plants, substantial quantities of ammonia are volatilized from the acid neutralizer, ammoniator-granulator, and dryer. Process economics require that ammonia be recovered.

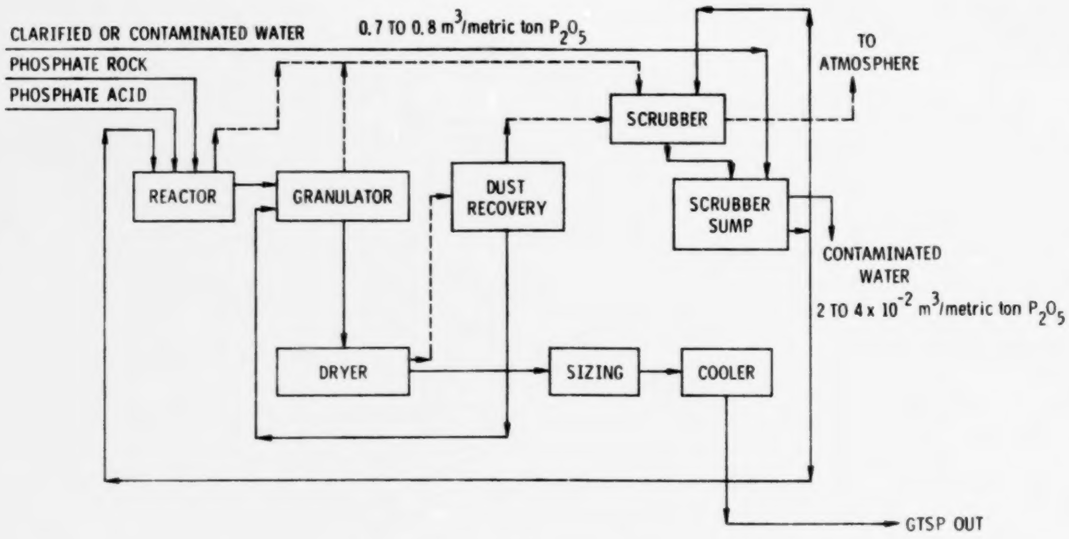
CLARIFIED OR CONTAMINATED WATER
0.7 TO 0.8 m^3/metric ton P_2O_5
PHOSPHATE ROCK
PHOSPHATE ACID
TO ATMOSPHERE
SCRUBBER
REACTOR
GRANULATOR
DUST RECOVERY
SCRUBBER SUMP
CONTAMINATED WATER
2 TO 4 x 10^{-2} m^3/metric ton P_2O_5
DRYER
SIZING
COOLER
GTSP OUT

Figure 54. ROP-TSP production (17).

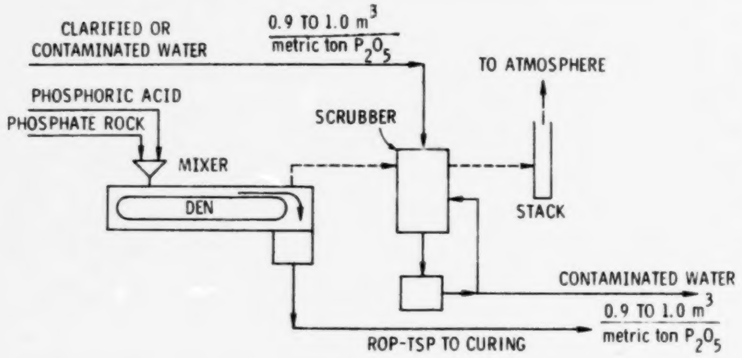
CLARIFIED OR CONTAMINATED WATER
0.9 TO 1.0 m^3 / metric ton P_2O_5
TO ATMOSPHERE
PHOSPHORIC ACID
PHOSPHATE ROCK
SCRUBBER
MIXER
DEN
STACK
CONTAMINATED WATER
0.9 TO 1.0 m^3 / metric ton P_2O_5
ROP-TSP TO CURING

Figure 55. GTSP production (17).

Weak (28% P_2O_5) phosphoric acid is used as the scrubbing liquor and is recycled back to the ammoniator-granulator (Figure 56). Phosphoric acid scrub solution is consumed in the process and therefore results in no effluent. However, the phosphoric acid scrub solution contains a small percentage of fluoride (1% to 3%), and optimum scrubber operation for ammonia recovery results in stripping of some of the fluoride from the acid. Secondary wet scrubber systems are occasionally used to further remove fluorides, particulates, ammonia, and combustion products from the neutralizer, granulator, dryer, cooler, and screening operations. This secondary scrubber system uses water as a scrubber liquor and is therefore a wastewater source. Scrubber effluents are contained in a water recycle system.

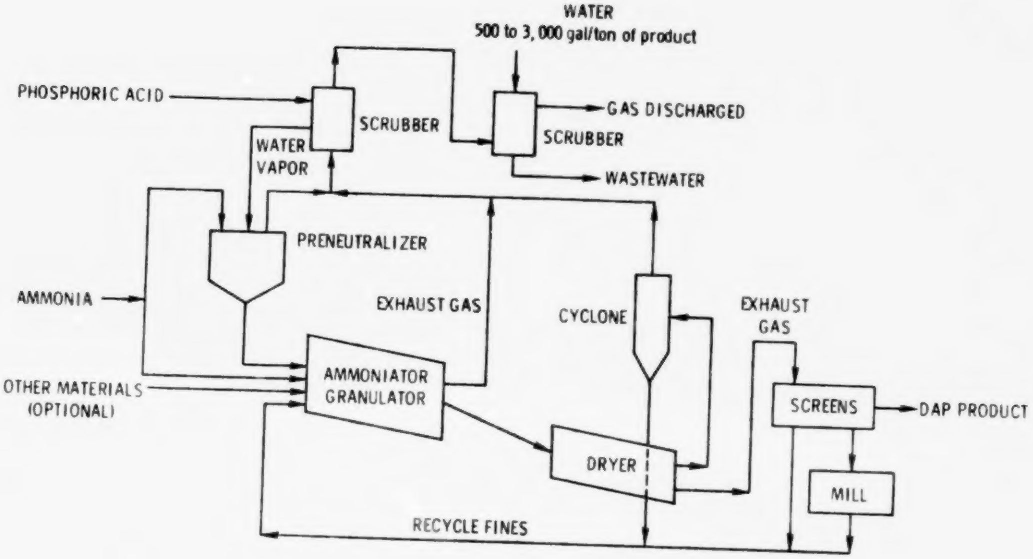
WATER
500 to 3,000 gal/ton of product
PHOSPHORIC ACID
SCRUBBER
WATER VAPOR
SCRUBBER
GAS DISCHARGED
WASTEWATER
PRENEUTRALIZER
AMMONIA
EXHAUST GAS
CYCLONE
EXHAUST GAS
OTHER MATERIALS (OPTIONAL)
AMMONIATOR GRANULATOR
SCREENS
DAP PRODUCT
DRYER
MILL
RECYCLE FINES

Figure 56. DAP production (4).

2. Nonpoint Sources

In phosphate fertilizer plants, various nonpoint sources can contribute to wastewater handling requirements.

a. Leaks and Spills--

In any plant, a certain number of valve and pump leaks as well as random spills can be expected. These leaks and spills are collected as part of the housekeeping procedure and, where possible, reintroduced directly to the process or contained in the contaminated water system. Spillage and leaks therefore do not normally represent a direct contamination of plant effluent streams that flow directly to natural drainage.

b. Runoff--

Rainfall runoff from a plant can collect quantities of contaminants from the ground and buildings at the production facility. Drainage from gypsum piles and mined-out areas at a phosphate fertilizer complex also may be a significant contributor to the overall water handling requirements of a plant. Runoff and drainage are collected and treated before discharge, if necessary, or sent to the contaminated water system for containment. Noncontaminated waters are kept segregated where possible and discharged without treatment.

c. Seepage--

The potential exists for chemical and radiological contamination of groundwaters as a result of seepage from gypsum stacks and large process water cooling ponds. Existing data is inconclusive and is insufficient to determine the possible extent of this contamination. The potential impacts due to seepage need to be determined on a site specific basis. Seepage can be reduced or prevented if it is a problem by lining ponds and underlaying gypsum piles with an impervious material.

3. Gypsum Pond

a. Gypsum Pond Characteristics--

The gypsum pond is an integral part of the wastewater treatment scheme at a typical phosphate fertilizer complex. The pond serves as a settling basin for gypsum (a byproduct of WPPA) and other waste solids, and it functions as a reservoir for recycling process water and cooling water. The size of the gypsum pond at a WPPA plant is approximately 2.23 x 10^{-3} km^2/metric ton P_2O_5/day (20). Gypsum ponds are located adjacent to the plant complex; they are, in many cases, abandoned phosphate rock mine pits.

Clarified gypsum pond water can be recycled for use in scrubbers and barometric condensers and for slurrying waste gypsum cake from the WPPA filtration process. With each recycle, the level of dissolved contaminants in the water increases. After 3 yr to 5 yr of recycle, impurities in pond waters approach equilibrium concentrations (20) which are a function of pH, temperature, and other chemical factors, and are maintained by volatilization and precipitation of impurities. Typical equilibrium concentrations are shown in Table 45 (17, 20).

TABLE 45. TYPICAL EQUILIBRIUM COMPOSITION OF GYPSUM POND WATER (17, 20)

Contaminant[a]	Concentration, g/m^3	Radioactivity, pCi/ℓ[b]
Phosphorus pentoxide	6,000 to 12,000	
Fluoride	3,000 to 10,000	
Sulfate	2,000 to 4,000	
Calcium	350 to 1,200	
Ammonia	0 to 100	
Nitrate	0 to 100	
Silica	1,600	
Aluminum	100 to 500	
Iron	70 to 300	
^{226}Ra		60 to 100

[a] The typical pH range is 1.0 to 1.8.

[b] Picocuries per liter; 1 picocurie equals 0.037 becquerel.

At pH less than 2, it is estimated that 80% of the phosphate present exists as phosphoric acid, the remaining 20% being the $H_2PO_4^-$ anion (20). The major equilibrium of fluoride componds as depicted in a model developed by Environmental Science and Engineering, Inc., is shown in Figure 57 (20). Data collected by remote sensing indicate that fluoride emissions from the gypsum pond

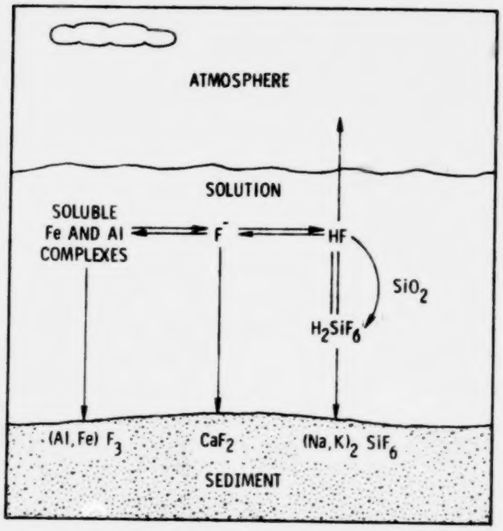
ATMOSPHERE
SOLUTION
SOLUBLE
Fe AND Al
COMPLEXES
F^-
HF
SiO_2
H_2SiF_6
$(Al,Fe)F_3$
CaF_2
$(Na,K)_2SiF_6$
SEDIMENT

Figure 57. Major gypsum pond equilibrium (20).

consisted entirely of hydrogen fluoride. The silicon tetrafluoride concentration was below the detectable threshold of 0.5 ppb (66). In addition to predominant compounds, fluosilicic acid (H_2SiF_6) and hydrogen fluoride (HF), small amounts of fluoride will be present in the water as soluble and insoluble aluminum and iron complexes.

b. Seepage Control from Gypsum Piles--
Natural soil from the surrounding area provides the base for dikes surrounding gypsum ponds. Gypsum is used to increase the height of the dike. A drainage ditch surrounds the perimeter of the area to control contaminated water seepage through earth and gypsum.

Design of the ditch is dependent on area geology and impoundment water level. Figures 58 and 59 show examples of dike (64) and seepage ditch construction. Water effluent collected is pumped from a low collection point in the ditch back into the pond.

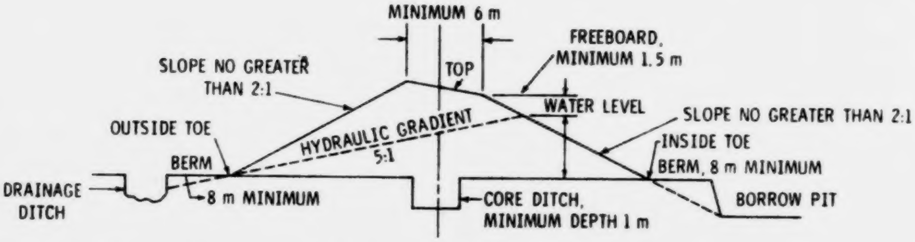
MINIMUM 6 m
FREEBOARD,
MINIMUM 1.5 m
SLOPE NO GREATER
THAN 2:1
TOP
WATER LEVEL
SLOPE NO GREATER THAN 2:1
OUTSIDE TOE
HYDRAULIC GRADIENT
5:1
INSIDE TOE
BERM
BERM, 8 m MINIMUM
DRAINAGE
DITCH
8 m MINIMUM
CORE DITCH,
MINIMUM DEPTH 1 m
BORROW PIT

Figure 58. Recommended minimum cross section of dam (64).
Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 506, by courtesy of Marcel Dekker, Inc.

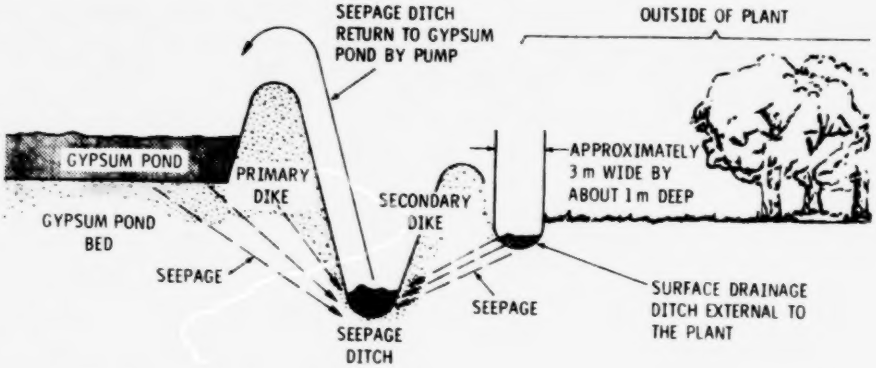
SEEPAGE DITCH RETURN TO GYPSUM POND BY PUMP
OUTSIDE OF PLANT
GYPSUM POND
PRIMARY DIKE
GYPSUM POND BED
SEEPAGE
SECONDARY DIKE
APPROXIMATELY 3 m WIDE BY ABOUT 1 m DEEP
SEEPAGE
SEEPAGE DITCH
SURFACE DRAINAGE DITCH EXTERNAL TO THE PLANT

Figure 59. Gypsum pond water seepage control (17).

c. Lime Treatment of Gypsum Pond Effluents--
Double or triple lime treatment of gypsum pond effluents is the only wastewater control technology used by the phosphate fertilizer industry, and it is practiced at only those plants that still discharge effluents. A schematic diagram of a two-stage lime treatment plant is shown in Figure 60.

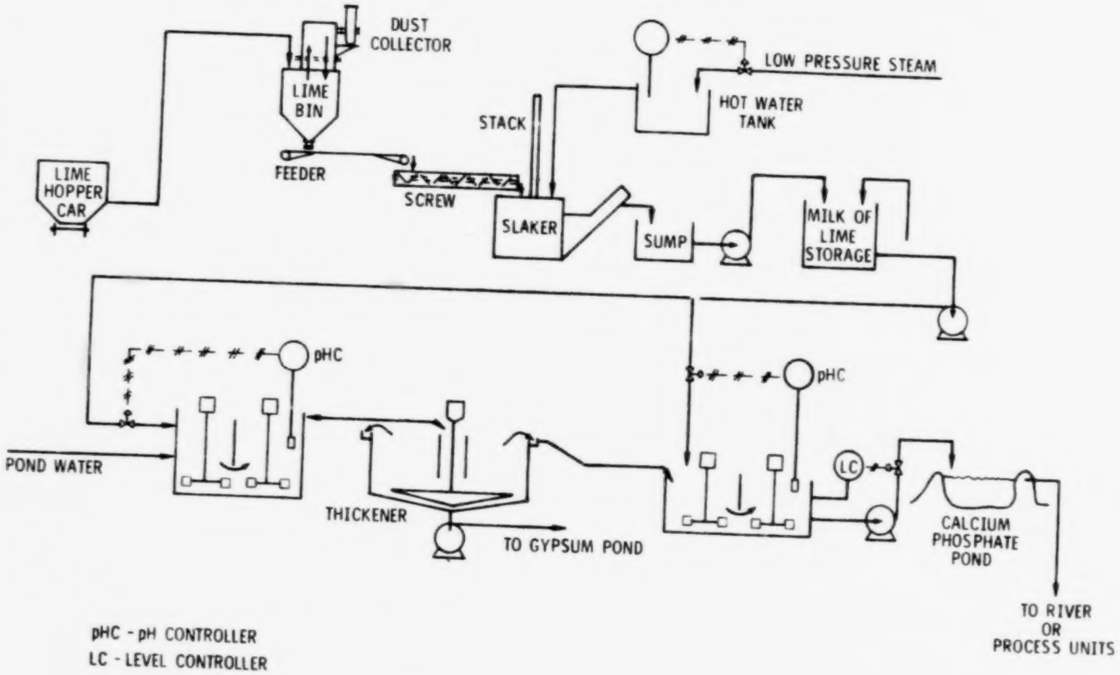
DUST COLLECTOR
LOW PRESSURE STEAM
LIME BIN
HOT WATER TANK
STACK
LIME HOPPER CAR
FEEDER
SCREW
SLAKER
SUMP
MILK OF LIME STORAGE
pHC
pHC
POND WATER
THICKENER
LC
TO GYPSUM POND
CALCIUM PHOSPHATE POND
TO RIVER OR PROCESS UNITS
pHC - pH CONTROLLER
LC - LEVEL CONTROLLER

Figure 60. Two-stage lime treatment plant (17).

At least two stages of liming are required; the first treatment raises pH from less than 2 to about pH 3.5 to about pH 4.0 (20).

As pH increases, availability of fluoride ions increases, as illustrated in Figure 61 (20). Calcium fluoride (CaF_2) precipitates according to the following reaction (20):

$$Ca^{++} + 2F^{-} \rightarrow CaF_2 \downarrow \qquad (38)$$

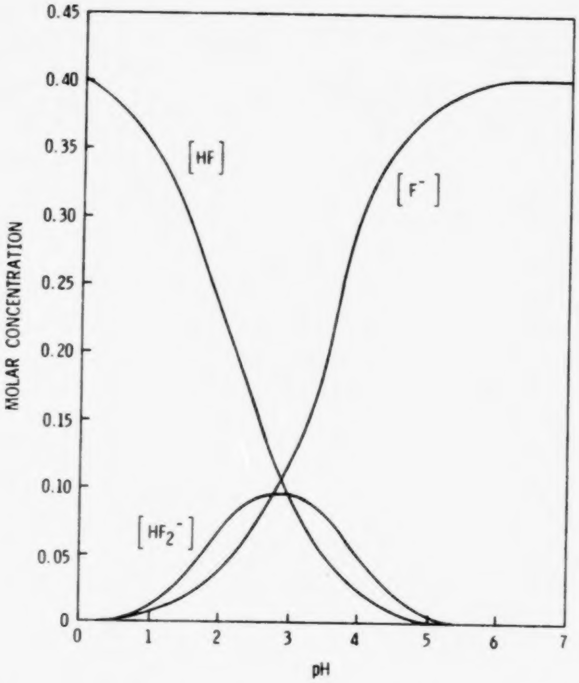

Figure 61. Species predominance diagram for 0.4 M hydrogen fluoride solution (20).

Another reaction also occurs, resulting in deposition of silica and calcium fluoride (20):

$$H_2SiF_6 + 3CaO + H_2O \rightarrow 3CaF_2 + 2H_2O + SiO_2 \qquad (39)$$

The second stage of lime treatment raises pH to greater than 6.0, with calcium phosphates precipitating via the following reactions (20):

$$2H_3PO_4 + CaO + H_2O \rightarrow Ca(H_2PO_4)_2 + 2H_2O \qquad (40)$$

$$Ca(H_2PO_4)_2 + CaO + H_2O \rightarrow 2CaHPO_4 \downarrow + 2H_2O \qquad (41)$$

Additional calcium fluoride will also precipitate.

Results of neutralizing a sample of gypsum pond water to a pH of 5.1 are given in Table 46 (28).

TABLE 46. REACTION OF GYPSUM POND WATER WITH LIME (28)

Calcium carbonate added			Chemical composition of filtrate, g/m³			
kg/m³	Percent of theoretical[a]	pH of filtrate[b]	Phosphorus pentoxide	Calcium oxide	Sulfate	Fluoride
0[c]	0	1.8	2,000	1,400	2,760	2,900
6.0	50	3.2	1,650	1,200	2,500	1,000
9.0	75	3.4	1,410	1,100	2,300	70
12.0	100	4.8	590	1,100	2,600	20
13.2	110	5.1	580	1,100	2,700	20
15.0	125	5.1	580	1,100	2,600	30
18.0	150	5.1	580	1,100	2,600	30

[a] Calcium carbonate required to react with fluorine and phosphate.
[b] Measured with Beckman glass electrode pH meter, Model H-2.
[c] Original gypsum pond water.

Laboratory data for phosphorus and fluoride removal at pH values over 5 are presented in Table 47 (17).

TABLE 47. LABORATORY DATA FOR PHOSPHORUS AND FLUORIDE REMOVAL AT HIGHER pH (17)

pH	Phosphorus, g/m³		Fluoride, g/m³	
	Laboratory	Plant	Laboratory	Plant
5.5				17
6.0		42		14
6.5		24		12.5
7.0	500	18	13	12.5
7.5	330	14	8.5	12.5
8.0	200	12	6.8	12.5
8.5	120	8	5.8	12.5
9.0	20	6	5.2	12.5
9.5	3	3	4.8	12.5
10.0	1.2	1.2	4.6	12.5

NOTE.—Blanks indicate data not available.

^{226}Ra is also precipitated by lime treatment with increasing pH as shown in Table 48.

TABLE 48. REMOVAL OF ^{226}Ra BY LIME TREATMENT (17)

pH	^{226}Ra, pCi/ℓ
2.0	91
1.5	65
4.0	7.6
8.0 to 8.5	0.04

"Double lime" treatment does not reduce nitrogen levels, although at high pH (greater than 9.0) significant ammonia loss to ambient air can occur (17). To date there is no proven means of economically removing ammonia nitrogen from aqueous solutions having low concentrations in the range of 20 to 60 g/m^3. The best control method is keeping the ammonia contaminant level low by preventing its entry into the main contaminated water system. This is accomplished to a great extent by scrubbing emissions from the ammonium phosphate production unit with a weak solution of phosphoric acid that is subsequently consumed in the process.

The main disadvantage of the liming operation for continual use is the high cost involved. Because the buffering capacity of the gypsum pond water is high at pH 1.0 to pH 3.0, large amounts of lime are required to raise the pH initially to 3.0 relative to the amount required to raise the pH from 3.0 to 6.0 (20). An additional disadvantage is the deposition of calcium fluoride on the lime particles, rendering them chemically inactive. The use of high intensity agitators is required to prevent this from happening.

An investigation was conducted specifically to evaluate the reduction in radionuclide levels in wastewaters by various lime treatment processes (14). In the initial treatment laboratory tests, process pond water was obtained from a Florida wet process facility, and four bases (quick lime, limestone, hydrated lime, and dolomite) were added to 4 ℓ of process water in different amounts to increase the pH. After vigorous agitation, the solutions were allowed to settle, and the resultant supernatant liquids were filtered and analyzed for their soluble ^{226}Ra concentrations. The results as presented in Table 49 show that in all treatment cases the soluble ^{226}Ra concentration was reduced by more than 99.7%, even though the final pH ranged from 4.0 to 8.0. This large reduction is attributed to the amount of readily available sulfate ions in the process water enabling large-scale coprecipitation of calcium-radium sulfate.

TABLE 49. LABORATORY PROCESS WATER TREATMENT STUDY (14)

Treatment	Amount of base added, g	Resultant pH	Dissolved ^{226}Ra, pCi/ℓ
Untreated process water	0	2.0	75.8[a]
Calcium oxide (quick lime)	70	7.9	0.15
Limestone rock	500	4.6	0.11
Slaked lime (hydrated lime)	50	8.0	0.07
Dolomite	500	4.0	0.16

[a] 6.7 pCi/ℓ undissolved.

Subsequently, field studies were conducted at several WPPA facilities to verify the effectiveness of lime treatment as observed in the laboratory (14). Results at four plants are presented in Table 50.

TABLE 50. EFFECT OF LIME TREATMENT ON RADIOACTIVITY REMOVAL FROM EFFLUENTS FROM A WPPA PLANT (14)

Sample	pH	Total ^{226}Ra, pCi/ℓ	Total uranium, pCi/ℓ			Total thorium, pCi/ℓ		
			^{234}U	^{235}U	^{238}U	^{228}Th	^{230}Th	^{232}Th
Plant A--Field Survey Number 1								
Untreated process water	2.0	82.3	1,086	48	1,045	2.5	70	4.5
Outfall (after double liming)	9.1	4.54	1.09	ND[a]	0.52	0.44	0.57	0.04
Plant A--Field Survey Number 2								
Untreated process water	1.8	55.6	411	24	394	3.4	101	3.2
Limed once	4.4	1.20	[b]	[b]	[b]	[b]	[b]	[b]
Prior to second liming	4.3	1.5	39.7	2.2	39.5	ND	0.52	ND
Outfall (after second liming)	7.1	1.8	16.8	0.98	16.8	0.32	0.71	0.11
Plant B--Field Survey Number 1								
Untreated process water	2	86.2	1,769	98.8	1,825	3.92	393	6.33
After first liming[c]	4.5	74.0	736	33.4	734	6.15	4.3	7.5
Prior to second liming	6	0.90	67.8	3.17	68.1	ND	1.32	ND
Outfall (after double liming)	8	0.45	0.26	ND	0.33	0.1	0.13	ND
Untreated nonprocess water	-[b]	1.38	0.28	ND	0.39	ND	ND	ND
Nonprocess water after liming	-[b]	2.6	0.96	ND	0.75	0.13	0.79	0.07
Nonprocess water outfall	-[b]	0.88	0.34	ND	0.42	ND	1.32	ND
Plant C--Field Survey Number 1								
Process water	1.9	55.2	676	35.1	661	0.86	8.6	4.1
Outfall (after single liming)	6.6	2.55	0.26	ND	0.28	ND	ND	ND

[a] None detected. [b] Not measured.

[c] These concentrations are high because of the large suspended solids load of 23.5 g/ℓ. The dissolved concentrations in picocuries per liter were 5.2 for ^{226}Ra, 12.8 for ^{234}U, 0.52 for ^{235}U, and 12.9 for ^{238}U.

Field survey number 1 at Plant A was conducted very early in the rainy season prior to the initiation of large-scale effluent treatment. Field survey number 2 was performed late in the rainy season after almost continuous lime treatment for over 2 mo. A comparison of process water from survey number 1 to survey number 2 shows a 32% decrease in ^{226}Ra concentration during the second survey. This is probably due to the combination of dilution of the process water by the influx of surface rain runoff and the removal of the radioactive material by treatment and discharge of approximately 10,000 cubic meters of water per day.

Results for every plant show that treatment with lime is highly efficient (greater than 94%) in removing ^{226}Ra from the discharged process water, in good agreement with removal efficiencies observed in the laboratory experiments. Lime treatment also proved to be extremely effective in removing uranium and ^{230}Th from treated process water, with removal efficiencies of at least 96% and 99%, respectively, in the four cases noted.

Therefore, although primarily designed for pH, phosphorus and fluoride control, not for removal of radionuclides in the effluent, treatment with lime was observed to be highly effective in removing ^{226}Ra, uranium, and thorium from the effluent discharge. These results are attributed to the following factors (14):

- Process water contains a large concentration of sulfate and phosphate ions to enable ready compound formation.

- Neutralization by an agent such as lime not only allows for the reduction of solubility of several compounds but provides an ample supply of calcium ions to enable the large-scale formation of calcium sulfate.

- The relative insolubility of radium sulfate makes it readily coprecipitate with calcium sulfate.

- Uranium and thorium probably precipitate along with calcium sulfate and other components through substitution for calcium in formed compounds.

- Settling provides the opportunity for the precipitated compounds to be removed from the effluent and not be discharged as suspended solids.

B. POTENTIAL ENVIRONMENTAL EFFECTS

1. Wastewater Disposal and Treatment Practices

Information about the extent of wastewater disposal and/or containment practices utilized by the phosphate fertilizer industry was obtained through industrial contacts. A summary of the wastewater handling practices is presented in Table 51. Contacts with over 70% of the plants in the industry revealed that nearly 75% have no discharge of process wastewater. Of the 15 plants that reported a discharge, 12 reported a discharge of treated process water only when necessitated by excessive rainfall. Several of these had not treated or discharged water for several years. In actual practice, discharge of contaminated process water from the recycle pond system is held to an absolute minimum due to the treatment cost involved.

Wastewater discharge practices have been restricted due to recently promulgated EPA regulations. Beginning July 1, 1977, and effective when each plant's wastewater discharge permits are subject to renewal, discharge of process wastewater pollutants to navigable waters is allowed only under the following conditions (79):

- Process wastewater impoundment facilities must be constructed to contain precipitation from the 10-yr, 24-hr rainfall event as established by the U.S. National Weather Service.

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(79) 40 CFR 418, Fertilizer Manufacturing Point Source Category, Subpart A--Phosphate Subcategory. Federal Register, 41(98): 20582-20585, 1976.

TABLE 51. WATER EFFLUENT DISPOSAL AND CONTAINMENT PRACTICES FOR THE PHOSPHATE FERTILIZER INDUSTRY
[percent of plants specified (number of plants)]

	Industry					
	Wet process phosphoric acid plants	Superphosphoric acid plants	Normal superphosphate plants	Triple superphosphate plants	Ammonium phosphate plants	Total phosphate fertilizer industry
Process water discharged continuously:						
Treated	7 (2)[a]	0 (0)	0 (0)[b]	7 (1)[a]	6 (2)[a]	3.1 (2)
Untreated	3 (1)[c]	0 (0)	0 (0)	0 (0)	0 (0)	1.5 (1)
Discharge of treated process water only when necessitated by excessive rainfall[d,e]	38 (11)[f]	44 (4)[f]	6 (2)	57 (8)[f]	38 (12)[f]	18.5 (12)
No discharge of process water reported	52 (15)	56 (5)	88 (27)	36 (5)	53 (17)	72.3 (47)
Insufficient information	0 (0)	0 (0)	6 (2)	0 (0)	3 (1)	4.6 (3)
Total	100 (29)	100 (9)	100 (31)	100 (14)	100 (32)	100 (65)
Pond system onsite for water containment and reuse:	90 (26)	89 (8)	36 (11)	100 (14)	84 (27)	
Continuous discharge from pond system	7 (2)[a]	0 (0)	0 (0)	7 (1)[a]	6 (2)[a]	
Discharge only when necessitated by periods of excessive rainfall	38 (11)	44 (4)	6 (2)	57 (8)	38 (12)	
No discharge from pond system reported	45 (13)	44 (4)	23 (7)	36 (5)	38 (12)	
Treat pond system with lime to precipitate fluorides and other contaminants	3 (1)	11 (1)	13 (4)	7 (1)	3 (1)	
Uncertain	0 (0)	0 (0)	6 (2)	0 (0)	3 (1)	
No pond system onsite	0 (0)	0 (0)	-[g]	0 (0)	3 (1)[h]	
Information regarding wastewater handling system incomplete	10 (3)	11 (1)	3 (1)	0 (0)	13 (4)	
Recover fluosilicic acid	28 (8)	0 (0)	61 (19)	0 (0)	0 (0)	
Number of plants contacted	29	9	51[i]	14	33[i]	
Number of plants in industry	36	9	66	16	48	
Percent of industry surveyed	81	100	77	88	69	

---

[a] Completion of proposed modifications to water recycle system in December 1977 at one plant will result in discharge of process wastewater only in event of excessive rainfall.

[b] One NSP plant that was found to discharge into a sewer system after neutralizing liquid wastes ceased production in 1975.

[c] One plant uses Mississippi River water on a once-through basis and discharges without treating (gypsum is impounded).

[d] Actual number may vary somewhat since some plants that report no discharge of process wastewater may in fact discharge in the event of an extremely rainy period.

[e] Many plants report no discharge of process wastewater necessary for 3 yr or more.

[f] One plant reported that excess water is double limed and sent to a mine for use and that no contaminated water will be allowed to enter navigable streams or public waters.

[g] Number of plants having no pond system onsite is uncertain, because NSP plants practicing fluorine recovery may still employ a small pond or reservoir.

[h] Ammonium phosphate production unit is located at a steel mill.

[i] Wastewater handling practices for those plants expected to close during 1976 or early 1977 were not included in survey.

- Process wastewater must be treated and discharged whenever the water level due to catastrophic precipitation events equals or exceeds the midpoint of the surge capacity.

- When such a discharge must occur, the pollutant concentrations must have 30-day average values of less than 35 g/m^3 of total phosphorus and 25 g/m^3 of fluoride.

2. Effluent Parameters

Wastewater from the manufacture of phosphate fertilizer materials originates from many point and nonpoint sources. The quantity and characteristics of a given plant effluent are dependent on the types of processes present at a complex, plant-to-plant variations in process design and operation, equipment age, level of maintenance, plant drainage and collection system, and wastewater treatment methods. As a result, it is difficult to define average effluent parameters that are truly representative of the industry as a whole. The approach taken in this study is to present available water discharge data for a representative number of the phosphate fertilizer complexes that report a discharge.

Justification for this approach is as follows:

- Thirteen of the fourteen ammonium phosphate plants that were found in the study to discharge wastewater are located at fertilizer complexes producing phosphoric acid. The one exception uses excess process water to irrigate pasture land. No other information is available concerning this plant. Another plant reporting a discharge of treated wastewater and not located at a phosphoric acid complex was expected to discontinue ammonium phosphate production in early 1977 and was not included in the survey results.

- All superphosphoric acid plants are located at complexes producing WPPA.

- Fifteen of the sixteen TSP plants are located at fertilizer complexes producing WPPA. The one exception was expected to close during calendar year 1976 or early 1977.

- The two NSP plants that reported a discharge of process water when necessitated by excessive rainfall are located at complexes producing phosphoric acid.

Available wastewater discharge data on file as of October 1976 at the Florida Department of Environmental Regulation in Winter Haven were collected and are presented in Table 52. Nonprocess water from a phosphate fertilizer plant may include any of the following: noncontact cooling water from the phosphoric acid

TABLE 52. WASTEWATER DISCHARGE DATA FOR PHOSPHATE FERTILIZER PLANTS

Plant code	Design production capacity, metric tons P_2O_5/day	Type of discharge	Reported treatment	pH, range (average)	Yearly average/daily maximum						Date
					Flow rate, m^3/s	Fluoride, g/m^3	Total suspended solids, g/m^3	Phosphorus, g/m^3	Ammonia-nitrogen, g/m^3	^{226}Ra, pCi/ℓ	
A	1,900	Process (pond)	Double limed.	5.6/11.7 (8.8)	0.41/0.21	20.1/49.0	21.8/71.0	43.1/330.0	32.6/82	2.6/6.2	7/75 to 6/76
		Nonprocess:									
		1	–[a]	6.2/11.7 (9.2)	0.29/0.61	4.38/14.0	3.7/18.0	0.8/12.1			7/75 to 6/76
		2		2.4/9.0 (7.4)	0.018/0.031	9.3/175	19.3/128	46.3/780			7/75 to 12/75
B	1,270	Pond[b]	Neutralize discharge.[c]	3.5/10.5	2.0/	28.5/225	68/267	25/55	7.4/149		Date unknown[d]
C[e]	272	Nonprocess	Lime treat if necessary.	/7.1 (6.7)	0.36/0.91	5.0/56	10/15	15.3/18.9			5/75 to 4/76
					0.36/	1.8/	6.6/	11.2			6/77 to 5/78
D[e]	535	Nonprocess[f]	Lime treat if necessary.	/7.5 (6.6)	0.18/0.44	8.2/12.8	8.5/14.1	21.0/37.2			4/75 to 4/76
					0.28/	6.3/	4.3/	12.1/			
E	381	Process (pond)[g]	Double limed.	5.6/11.4	0.0013/	39.2/183	172/	52.9/	8.8/		1973
		Seepage (pond)		3.6/6.2	0.000020/	3,381/6,500	20.8/	39/			
		Nonprocess		5.5/10.2	0.027/	4.0/42.5	10/	4.9/	3.6/		
F	907	Nonprocess[h, i]	Allowed to settle before discharge.	/8.0 (5.4)	0.025/0.11	1.66/5.1	15.5/58	2.56/4.8			7/75 to 7/76
G	363	Process (pond)[j]	Neutralize and discharge.[k]	/10.54 (3.37)	0.45/0.69	8.4/27.0	21.9/215	15.3/128			6/75 to 5/76

[a] Blanks indicate information not available. [b] All wastewater enters pond system. [c] New wastewater handling system now used. [d] Early 1970's.

[e] More recent effluent data supplied by plant personnel. [f] Zero discharge of process water from pond system practiced.

[g] Last discharge of process water occurred in 1975; as of October 1976 discharge of process water only during period of excessive rainfall.

[h] Discharge of pond water only in period of extreme rainfall. [i] No discharge of pond water required in previous 5-yr period.

[j] All water enters pond system. [k] Modifications to existing wastewater handling system completed December 1977. Will discharge from pond only during period of heavy rainfall after double limining in future.

production unit, cooling tower blowdown from an associated sulfuric acid plant, rainfall runoff, drainage from mined-out areas, washdown waters, and spills.

3. Source Severity

For water effluents source severity compares the concentration of a particular pollutant after discharge and dilution in the receiving body with an estimated allowable concentration denoted as the hazard factor. The concepts of hazard factor and severity are used as a basis for comparison of the relative impacts of a large number of source types. The hazard factors used in this evaluation may be changed as better health effects data becomes available.

In determining the source severity of a plant, the discharge quantity is compared to the receiving body flow rate times the hazard factor according to Equation 42.

$$S = \frac{V_D C_D}{V_R + V_D \; F} \tag{42}$$

where S = source severity for a particular pollutant

V_D = wastewater effluent flow rate, m^3/s

C_D = concentration of particular pollutant, g/m^3

V_R = volumetric flow rate of receiving body above plant discharge, m^3/s

F = hazard factor for particular pollutant, g/m^3

Hazard factors for individual pollutants are given in Table 53 (80-82).

A value of 1.00 g/m^3 was used for the ammonia-nitrogen present in the wastewater effluent because at a pH of 7 or lower, nearly 100% of the ammonia-nitrogen exists in the ionized form.

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(80) Quality Criteria for Water. EPA-440/9-76-023, U.S. Environmental Protection Agency, Washington, D.C., 1976. pp. 16-21.

(81) Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. EPA-600/8-77-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1977. 73 pp.

(82) Eimutis, E. C., J. L. Delaney, T. J. Hoogheem, S. R. Archer, J. C. Ochsner, W. R. McCurley, T. W. Hughes, and R. P. Quill. Source Assessment: Prioritization of Stationary Water Pollution Sources. EPA-600/2-77-107p, U.S. Environmental Protection Agency, Washington, D.C., December 1977. 119 pp.

TABLE 53. HAZARD FACTORS (80-82)

Effluent species	Hazard factor
	g/m³
Fluoride	0.19
Total suspended solids	25
Phosphate-phosphorus	0.10
Ammonia-nitrogen (ionized form)	1.00
	pCi/ℓ
^{226}Ra	5

Discharge data presented in Table 52 were used to calculate source severity values. Source severities for individual phosphate fertilizer complexes are presented in Table 54. Only one set of eight measurements for ^{226}Ra contamination in discharged process waters was available. The low severity determined for this case along with the information presented in Table 48 for radium precipitation with increasing pH suggest that the severity due to this contaminant will remain extremely low in effluent streams treated with lime to remove fluorides and phosphates. Source severities for fluoride, phosphorus, and to a lesser degree ammonia-nitrogen are in a number of cases greater than 1.0. This is due to the low flow rate (1 m^3/s to 6 m^3/s) of the receiving bodies (83). By comparison, the mean flow rate of the Ohio River at Greenup, Kentucky, is 3,210 m^3/s (84).

In addition to the effects from normal wastewater discharge, there is a potential danger from dike failure around a gypsum pond. Such failures have occurred in the past and have resulted in large fish kills when untreated pond waters were discharged directly into surface streams. Dikes are now constructed to prevent this from happening; thus, there is no way to evaluate the chances of future dike failures.

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(83) Water Resources Data for Florida, Water Year 1975. Volume 3--West-Central Florida Surface Water, Ground Water, Quality of Water. USGS-WRD-FL-75-3 (PB 259 493), U.S. Department of Commerce, Tallahassee, Florida, July 1976. 1249 pp.

(84) Water Resources Data for Kentucky, Water Year 1975. USGS-WDR-KY-75-1 (PB 251 853), U.S. Department of Commerce, Louisville, Kentucky, January 1976. 348 pp.

TABLE 54. SOURCE SEVERITIES FOR WASTEWATER DISCHARGES AT INDIVIDUAL PHOSPHATE FERTILIZER COMPLEXES

Plant code	Receiving body	Type of discharge	Mean flow rate of receiving body,[a] m^3/s (82)	Source severities[b]				
				Fluoride	Total suspended solids	Phosphorus	Ammonia-nitrogen	Radium
A	North Prong, Alafia River	Process (pond)	2.97	1.43	0.012	5.82	0.44	0.007
		Nonprocess		2.3	0.018	3.2	-[c]	-
		Combined		3.59	0.028	8.44	-	-
B	North Prong, Alafia River	Pond[d]	2.97	11.6	0.20	19.3	0.57	-
C	Peace River	Nonprocess[e]	1.02	6.86	0.10	39.9	-	-
				2.47	0.069	-	-	-
D	Peace River	Nonprocess[e]	1.02	6.47	0.051	31.5	-	-
				7.14	0.037	26.1	-	-
E	North Prong, Alafia River	Process (pond)	2.97	0.089	0.0030	0.227	0.0038	-
		Seepage (pond)		0.12	0.0000058	0.00273	-	-
		Nonprocess		0.19	0.0036	0.44	0.32	-
		Combined		0.40	0.0065	0.67	0.36	-
F	Skinned Sappling Creek to Alafia River	Nonprocess	6.14[g]	0.035[g]	0.0025[g]	0.102[g]	-	-
G	Thirty Mile Creek to North Prong, Alafia River	Process Pond	2.97[i]	5.75[i]	0.11[i]	19.9[i]	-	-

[a] Mean of daily averages for the 1975 water year (October 1974 to September 1975).

[b] Average discharge rates and contaminant levels used in severity calculations.

[c] Dashes indicate that information not reported or that insufficient information was available to perform calculation.

[d] All wastewater enters pond system.

[e] Zero discharge of process water from pond system practiced.

[f] Discharge of process water from pond system only in event of extreme rainfall period.

[g] Based on information available for the Alafia River since flow data for Skinned Sappling Creek are not reported.

[h] All water enters pond system.

[i] Based on information available for the North Prong of the Alafia River since flow data for Thirty Mile Creek are not reported.

SECTION 6

SOLID RESIDUE

A. SOURCES OF SOLID RESIDUE

Solid residue wastes are generated at phosphate fertilizer plants in the form of sludges and other slurries. These suspensions are sent to the gypsum pond or other settling basin where solids settle. The settled mass is either left in the pond, dredged for use in extending the dike, or recovered as a resource.

There are three sources of solid residue in the phosphate fertilizer industry:

- Gypsum from the filtration of wet process phosphoric acid.
- WPPA sludge.
- Wet scrubber liquor.

Gypsum ($CaSO_4 \cdot 2H_2O$), a byproduct in WPPA manufacture, is formed by reaction of phosphate rock with aqueous sulfuric acid:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightleftarrows 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O) \quad (43)$$

Reactant slurry flows from the acidulator to the filtration unit, where phosphoric acid is drawn off by vacuum filtration, leaving gypsum cake on the filter. Cake is washed with weak phosphoric acid to recover its residual acid and then rinsed from the filter screens with recycled pond water. Gypsum slurry flows to the gypsum pond for solids settling. In areas where land stability or availability prevents the use of ponds, gypsum cake from the filters is transported by conveyor to gypsum piles.

The quantity of gypsum produced in a WPPA plant ranges from 4.6 to 5.2 metric tons of gypsum/metric ton P_2O_5 produced (24, 64). As a rule of thumb, approximately 1,360 m^3 of gypsum will be accumulated yearly per metric ton of P_2O_5 produced per day (24).

A second source of solid residue is phosphoric acid from which impurity-bearing minerals settle out in the clarifier to form acid sludges. Phosphate rock salts which contribute to acid sludge formation include fluorine, iron, aluminum, silicon, sodium, and potassium salts. Table 55 shows an analysis of solids collected at various stages of WPPA acid production (22).

TABLE 55. ANALYSIS OF SOLIDS FROM WPPA (22)

Reprinted from Phosphoric Acid, Volume I, A. V. Slack, editor, p. 694, by courtesy of Marcel Dekker, Inc.

Solids from	Analysis, weight percent						
	Phosphorus pentoxide	Calcium	Sulfate	Aluminum	Iron	Fluorine	Silica
32% P_2O_5 acid (feed to evaporators)	1.9	14.8	38.9	0.3	0.2	19.9	10.3
54% P_2O_5 acid from evaporators	6.8	12.9	29.0	5.1	0.3	22.0	5.3
54% P_2O_5 acid from storage	38.9	3.3	4.7	1.5	9.6	12.9	6.1

Fluosilicates, fluorides, silica, cryolite [(Na or K)$_3$AlF$_6$], sulfates, unreacted phosphate rock, and various other combinations of impurities as complex salts have been identified in acid sludge (22).

Acid sludge is separated from acid in the clarification process. Separated solids can be either dried and used as a fertilizer or sent to the gypsum pond. Effluent from the clarification process ranges from 0.7 m^3 to 3.2 m^3/metric ton P_2O_5 (17).

The third source of solid residue wastes is wet scrubber liquor. Wet scrubbers are used throughout the phosphate fertilizer industry to remove particulates and fluorides from exhaust gas streams. Recycled gypsum pond water is used as scrubbing solution. After passing through the wet scrubber, solution is recycled back to the gypsum pond for solids settling.

At ammonium phosphate plants, for example, scrubber liquor going to the gypsum pond contains about 10 g of solid residue per kilogram of P_2O_5. This solid residue (20) is primarily silicon hydroxide ($Si[OH]_4$). The solids value is calculated on the basis of a filtered-to-concentrated phosphoric acid ratio of 1:1, assuming that all the fluorine from the acid goes to the exhaust gas stream as silicon tetrafluoride and that 85% of silicon tetrafluoride is collected in the scrubbing system. These solids will be deposited in the gypsum pond.

Although solid residue values for wet scrubber systems at other phosphate fertilizer operations do not exist, they should be similar to those for ammonium phosphate plants.

B. POTENTIAL ENVIRONMENTAL EFFECTS

Approximately 99% of solid residue wastes generated at phosphate fertilizer plants are stored in ponds, stacked in piles, or stored in mining pits at the plant site. The remaining 1% is sold as a raw material for various products.

Rainfall drainage from gypsum piles is collected in a ditch and recycled to the gypsum pond. Therefore, under normal conditions there will be no adverse environmental effect due to solid residues. The only concern due to these wastes is the large amount of land area required to store gypsum and the unsightly appearance of 30-m piles of gypsum.

To date, there are no data with which to evaluate potential effects on groundwater due to leaching from gypsum piles. Since gypsum wastes contain mainly calcium sulfate and lesser quantities of phosphates and fluorides, any potential adverse effect should be minimal.

There are no data available to estimate air emissions from gypsum piles due to wind erosion. However, this effect is minimal; layers of clay are applied to the surface of the gypsum for added strength when the material is used for dikes. Also, gypsum is listed as a nuisance dust with a corresponding inhalation TLV of 10 mg/m^3 of air (70).

C. CONTROL TECHNOLOGY

1. Disposal Practices

Waste gypsum produced in a WPPA plant ranges from 4.6 to 5.2 metric tons gypsum per metric ton of P_2O_5 produced (24, 64). Approximately 1,360 m^3 of gypsum will be accumulated yearly per metric ton of P_2O_5 produced per day so that at least 2,230 m^2 of land area per daily metric ton P_2O_5 should be reserved for gypsum disposal.

In the United States and other locations, three disposal practices are currently used: 1) gypsum ponds and piles, 2) abandoned mine pits, and 3) sea disposal. In the United States, more than 90% of the plants use gypsum ponds to collect slurry. Initially, two or more areas are converted to lagoons by means of low dikes provided with proper outfalls for potential effluent discharge. As one area becomes filled, the gypsum stream is diverted to the second area, and the first section is allowed to dry out sufficiently to support mechanical equipment. The dike is then increased in height using deposited gypsum as raw material, and the procedure is repeated. Existing gypsum piles range in height from 30 m to 36 m (17, 24).

In western states where poor land stability or availability prevents using gypsum ponds, gypsum cake from the vacuum filters is transported by conveyor to gypsum piles.

The second disposal technique is practiced primarily in Florida. Instead of constructing gypsum ponds, abandoned phosphate rock surface mines are used as gypsum ponds and for other solid residue disposal. The only potential environmental hazard from this disposal technique is possible leaching of fluorides, phosphates, and 226 Ra into groundwater systems. The potential for such leaching to occur is presently unknown.

A third disposal technique, used by less than 2% of phosphate fertilizer plants in the United States but more widely used throughout Europe, is practiced at plants located in coastal areas. After removal from the vacuum filters, gypsum is slurried with about a tenfold quantity of seawater or cooling water. It is then pumped into the ocean, or, in a few cases, discharged into major rivers (64).

Seawater is a better solvent for gypsum than freshwater. Solubility of gypsum in seawater is about 3,500 g/m^3 as compared to about 2,300 g/m^3 in fresh water. The solids content of the gypsum slurry is below 5%, low enough for quick dispersion and dissolution in ocean water (64).

2. Resource Recovery

Several approaches have been taken in seeking commercial uses for waste gypsum and its associated solid residues. In 1975, approximately 30 x 10^6 metric tons of gypsum waste were generated by the phosphate fertilizer industry (85). Of this total, about 90 x 10^3 metric tons were applied to calcium-deficient soil in the southern states for peanut growing. Gypsum was also used for improvement of alkali soils in California and for land reclamation in coastal areas.

Because gypsum waste, often referred to as phosphogypsum (86), contains varying quantitites of phosphoric acid, it also serves as a light fertilizer.

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(85) Personal communication with John Sweeney, U.S. Bureau of Mines, Tallahassee, Florida, 26 September 1977.

(86) Murakami, K. By-product Recovery, As Raw Material for Plaster and Cement - Japanese Practice. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 519-523.

Waste gypsum has been used for wallboard. In the United States, however, the dihydrate process for phosphoric acid production produces a gypsum waste high in phosphoric acid which results in poor quality wallboard. Also, there is some concern about possible low-level radiation effects from wallboard made of uranium- and radium-containing gypsum wastes.

In Europe and Japan where the hemihydrate process is more commonly used, the resulting gypsum waste is purer, containing less phosphoric acid and uranium. More of this gypsum waste is used for wallboard. In England, where only the standard dihydrate process is used, special purification methods make the byproduct suitable for wallboard. This purification step is more economically feasible in England than in the United States because natural (and purer) gypsum is not as abundant in England as it is in the United States (27).

Another possible use for gypsum is in cement and other road toppings. However, the phosphoric acid and other phosphates retard setting and lower the strength of the hardened body. Fluorine compounds reduce setting time and lower the concrete strength, but these effects are small compared to the effects of phosphate contamination (86). In Florida, there are further concerns over public exposure to low-level radiation from road surfaces containing gypsum wastes or from road base material containing phosphate rock mining overburden.

Gypsum can be reacted with ammonia and carbon dioxide to form ammonium sulfate and calcium carbonate. This is an old and well-known practice applied to natural gypsum, but there has been relatively little application to waste gypsum. Only a few plants in India, Japan, and Europe use this technology (27).

Another potential resource recovery method is treating waste gypsum with silica at high temperatures to produce sulfuric acid. Furthermore, the additional product of calcium silicate could be used for cement. Although the method is technically feasible, the high water content of gypsum, the corrosive effect of fluorides, and the adverse effect of P_2O_5 content on cement quality are all major drawbacks. Moreover, due to the price and availability of sulfur in the United States, this technology is not yet economically feasible (27).

While several potential resource recovery methods are technically feasible, less than 1% of the gypsum waste in the United States is utilized because its recovery is not economically feasible and its disposal does not pose an environmental hazard. The remaining quantity is stored in piles near the plants.

SECTION 7

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

The recent trend in WPPA manufacture has been toward larger capacity, enclosed producing units with closer control of operating variables. Single, multicompartment tanks have replaced the earlier multiple tank systems and increased capacities from the older design capabilities of 180 to 270 metric tons P_2O_5 per day. Today a modern plant can produce 450 to 1,100 metric tons P_2O_5 daily (17). Improved engineering design and materials of construction have decreased capital and operating costs per unit capacity and have improved overall operating efficiency in WPPA manufacture. Recent production rates for WPPA are shown in Figure 62.

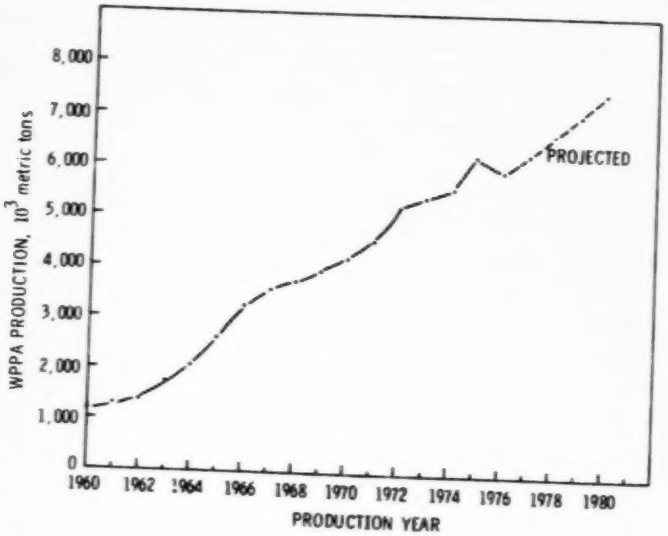

Figure 62. WPPA production trend (3).

NSP was, for many years, the major agricultural source of phosphate nutrient. In 1947 NSP accounted for over 90% of the total domestic supply. Since the mid 1950's, however, the popularity of NSP has undergone a sharp decline, and only in the past few years has the rate of decline started to moderate. Production has fallen steadily from 1,150,000 metric tons (P_2O_5) in 1960 to 439,000 metric tons in 1975 (9, 33). NSP consumption data are shown in Figure 63. The number of plants manufacturing NSP has shown a similar drop, from an estimated 200 plants located throughout the United States in the mid 1960's to 66 plants in 1975. The major reason for this decline is the poor economics of converting phosphate rock to a lower analysis material (NSP) with the associated increased cost of transportation per metric ton of nutrient--as compared with the production and distribution of the same phosphate values via more concentrated products.

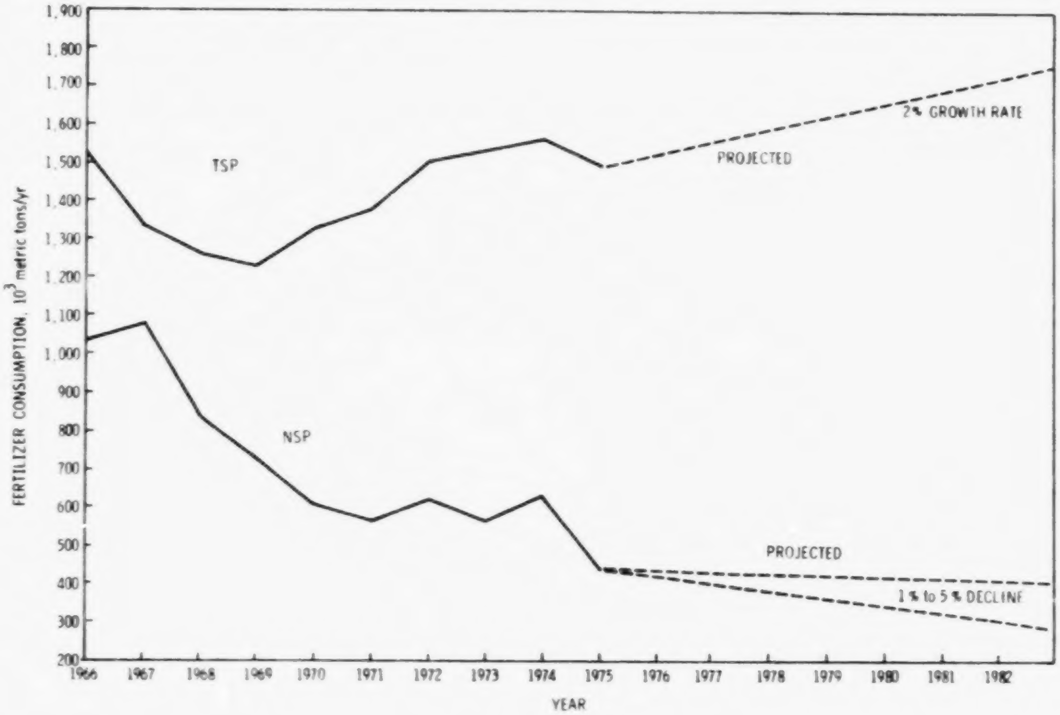

Figure 63. Superphosphate fertilizer consumption from 1966 to 1982 (29).

The simplicity of the NSP production process will act as a moderating influence in the continued decline of NSP output. NSP can be manufactured in small, inexpensive plants with low production costs per ton of P_2O_5 since calcium sulfate ($CaSO_4$) formed in the acidulation of the rock is not separated from the final product as in WPPA manufacture. The process is simple and easy to operate and requires less sulfuric acid per metric ton of P_2O_5 than does WPPA production.

TSP consumption in the United States has undergone a very rapid growth during the past quarter century. Recent consumption data are shown in Figure 64. Production has shown a fivefold increase in the period from 1950 to 1975. In 1975 an estimated 1,496,000 metric tons (100% P_2O_5 basis) were manufactured (9).

In the period from 1950 to 1965 TSP, with its higher P_2O_5 content, took over much of the market lost by NSP. Since 1966, TSP has typically represented 25% to 35% of the total annual domestic P_2O_5 fertilizer supply. At the present time, TSP is the second leading source of fertilizer phosphate (9). Although TSP production has maintained a moderate growth rate, it has declined in importance relative to ammonium phsophate because the latter has grown at a much faster rate.

The market for ammonium phosphate has expanded at the expense of the declining NSP and TSP market as shown in Table 56. From zero in 1950, the market share for ammonium phosphates grew to 14.3% in 1960 and 46.1% in 1970. Annual production and capacity data are shown in Figure 64.

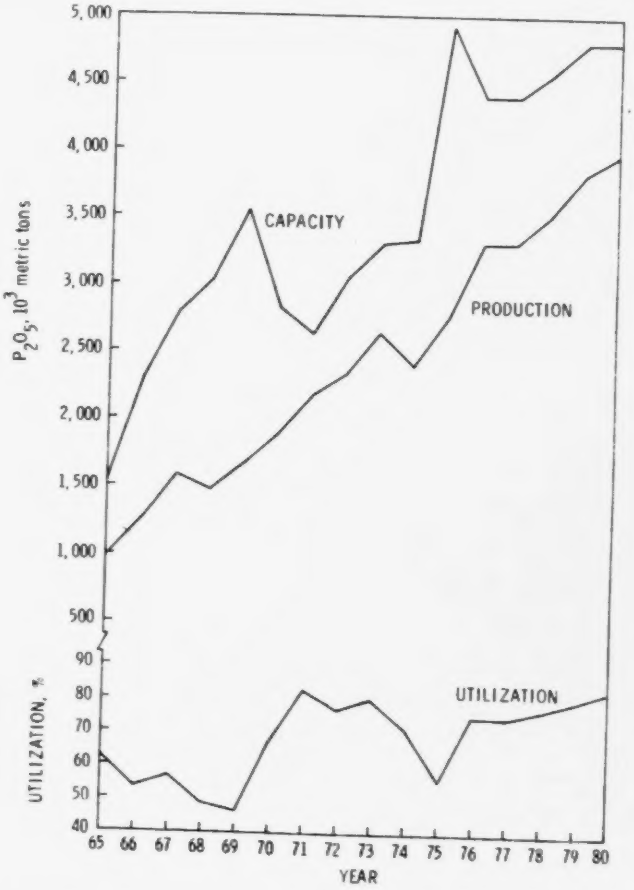

Figure 64. Ammonium phosphate capacity, production, and plant utilization projections to 1980 (7, 9-11, 34).

TABLE 56. DISTRIBUTION OF PHOSPHATIC FERTILIZER MATERIALS (47)

	Percentage of fertilizer market				
	1950	1960	1970	1980	2000
Normal superphosphates	85	46.4	13.5	4.1	1.5
Triple superphosphates	15	35.7	26.9	20.2	19.5
Ammonium phosphates	0	14.3	46.1	58.1	50.7
Others[a]	0	3.6	13.5	17.6	28.3
Total	100	100	100	100	100

[a] Growth in other phosphatic fertilizers is primarily superphosphoric acid, a main supplier to the liquid fertilizer market.

During a study of the ammonium phosphate industry to determine water discharge practices, several plants were found that no longer produced ammonium phosphates in 1977. A list of these plants is presented in Table 57. Had these plants been closed in 1975, nationwide capacity would have been 500,000 metric tons P_2O_5 lower, but production would have remained the same. Plant utilization for 1975 would have been 63% instead of the reported 56%; the mean annual plant capacity would have been 116,000 metric tons P_2O_5 instead of 103,000 metric tons P_2O_5; the average annual utilization rate would have been 74% instead of 73%; and all severities would have been 14% greater.

TABLE 57. PLANTS IDENTIFIED AS NO LONGER OPERATING IN 1977

Company	Location	1975 Capacity, 10^3 metric tons P_2O_5
Farmland Industries, Inc.	Joplin, MO	84
Gardinier, Inc.	Helena, AR	45
Kaiser Aluminum & Chemical	Wendover, UT	14
Kaiser Steel	Fontana, CA	14
Mississippi Chemical Corp.	Pascagoula, MS	139
Pennzoil Co.	Hanford, CA	Unknown
Standard Oil of California	Fort Madison, IA	73
	Kennewick, WA	27
	Richmond, CA	36
USS Agri-Chemicals	Cherokee, AL	68
Total	10 plants	500

B. EMERGING TECHNOLOGY

The higher energy requirement for production of thermal process phosphoric acid has caused investigation of processes to improve the purity of WPPA. The wet process requires about one-fifth of the energy per ton of product required in the thermal process (78). Because of the high cost and uncertainty of electric power, immediate expansion of the thermal process is not foreseen (78). Growth in the marketing areas of thermal acid will likely be met by improved quality WPPA. Although new cleanup processes do not produce food-grade acid, the improved quality acid can be used in detergent and animal feed applications.

A chemical method for purification of 32% wet process acid involves neutralization and precipitation of impurities, producing acid of detergent phosphate specifications. The two-stage neutralization process generates three vapor streams and two filter cake effluents (78). One plant, Olin Corp. in Joliet, Illinois, uses this process to produce sodium phosphates.

A second method of cleanup involves solvent extraction. The P_2O_5 content of the impure aqueous solution of phosphoric acid made by the wet process is extracted with an immiscible organic solvent; e.g., *n*-butanol. Impurities are left behind in the aqueous layer, and regeneration of the phosphoric acid is accomplished by contacting the organic phase with fresh water (22).

Fluorine liberated in the production of phosphate fertilizers could constitute a major supply of fluorine as deposits of fluorspar and cryolite are depleted. More restrictive and expensive fluoride control requirements are increasing emphasis on the potential value of waste fluorides, and increased effort in recovery of salable byproducts is expected (22).

The market for TSP for the near future is expected to remain relatively constant primarily due to the tremendous growth of ammonium phosphate. Currently the major source of fertilizer phosphate in the United States, ammonium phosphates are produced by reacting phosphoric acid with ammonia. Eighty-four percent of ammonium phosphate production is in the form of DAP. The increased use of DAP is attributable to several factors. It has a high water solubility, high analysis (18% N and 46% P_2O_5), good physical characteristics, and low production cost. In addition, the phosphate content of DAP (46%) is as high as that of TSP, so that by comparison the 18 units of nitrogen can be shipped at no cost.

The most likely new phosphate material to become available in the next few years is ammonium polyphosphate (APP) made from merchant-grade WPPA. Its market potential is based upon the likelihood that its production economics can be competitive with those of DAP and that it will be useful as a base for liquid and suspension fertilizers. The nutrient analysis for APP (12-57-0) is higher than that of DAP, and APP has demonstrated good storage and handling properties. APP has been made in pilot plant studies at TVA by reacting merchant-grade WPPA in a two-step reaction system. The second stage is a pipe reactor in which a melt is formed. The melt passes through a vapor disengagement vessel and is discharged into a pugmill for granulation (87).

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(87) Phillips, A. B. New Products for the Future. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 23-27.

C. INDUSTRY PRODUCTION TRENDS

The fertilizer segment of the phosphoric acid industry is currently facing a domestic overcapacity due to a number of new plants that have either come on stream or are expected within the next year or two. If U.S. agricultural commodity exports are expanded and sustained on a long-term basis, the upswing could help ease the overcapacity. Between 1974 and 1980, wet acid capacity will have increased by 56% while, over the same time period, total domestic demand is expected to grow by 44% to 54%. This results in an annual increase in production of 4% to 7% (Figure 62).

A shift from furnace phosphoric acid to WPPA is evident for production of sodium polyphosphates (used in detergents) and some animal feeds. The high energy and pollution control requirements for thermal phosphoric acid have also stimulated this trend. Growth in these areas would somewhat lessen the overcapacity problems caused by recent lower-than-expected demand for phosphate fertilizers.

Superphosphoric acid has a number of advantages over the more dilute 54% P_2O_5 phosphoric acid, and growth in this area is promising. The foremost advantage of super acid is shipping economy. A 7% to 10% average annual growth rate between 1977 and 1980 is projected in Figure 65.

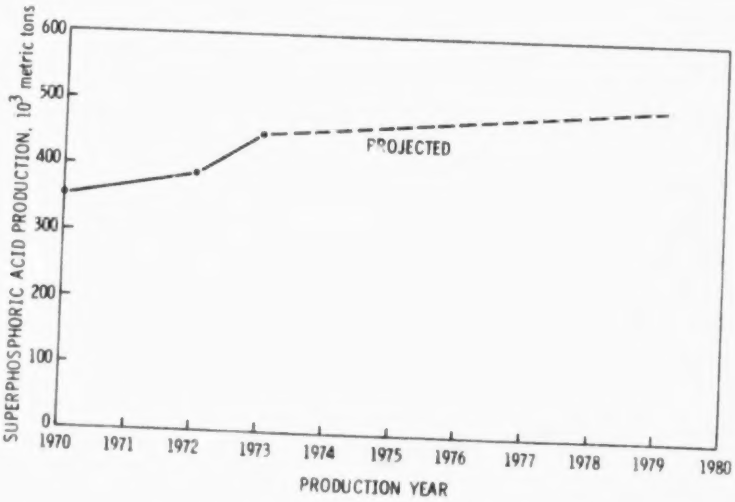

Figure 65. Superphosphoric acid production trend (3).

Total production of superphosphates and other phosphatic fertilizer materials in 1975 was 4,896,000 metric tons (100% P_2O_5), a slight increase over the 4,870,000 metric tons produced in 1974 (9). Production of NSP accounted for 9% of the total, a decline of 4% from the preceding year. TSP, on the other hand, has maintained a nearly constant share of the phosphatic fertilizer market of 25% to 35% for the 9-yr period dating from 1967 to 1975 (29). The future growth in the phosphate fertilizer industry is shown in Figure 63.

Declining demand for ROP-NSP and ROP-TSP is forecast (29). This prediction is based on an expected continued growth of mechanical blends of granulated concentrates (DAP, GTSP) and a further decline of N-P-K fertilizers produced at ammoniator-granulator plants (5). N-P-K ammoniator-granulator plants are primary consumers of ROP superphosphate materials. In addition, a shift in raw material usage for N-P-K plants is expected. Consumption of superphosphoric acid as a preferred phosphate source is expected to expand at the expense of NSP and TSP. The more concentrated superphosphoric acid (70% to 72% P_2O_5) provides economy by minimizing shipping costs. An annual decline of from 1% to 5% is predicted for NSP fertilizers.

GTSP will continue as a preferred phosphate source in low- and no-nitrogen mixed fertilizer blends. TSP production (within the limits of current technology) serves as the most convenient means of "disposing" of high-sludge-containing phosphoric acids. Production of sludge acids will maintain the incentive for steady or expanded output of GTSP.

As a result of all the preceding factors, TSP production is expected to experience an average annual growth rate of from 1% to 3%. The growth in GTSP production will be at least partially offset by a decline in ROP-TSP production.

Ammonium phosphate popularity as a fertilizer material is projected to result in continued growth of production and share of the phosphatic fertilizer market until the 1980's (Figure 64). From 1975 to 1980, production is projected to grow at an annual pace of approximately 7.5%, while capacity is estimated to decline at an annual rate of approximately 0.5% over the same period. The net result will be an increase in plant utilization rate from 56% to 83%. Ammonium phosphate's share of the phosphate fertilizer market is projected to be 58.1% in 1980 and 50.7% in 2000 (47) as shown in Table 56.

REFERENCES

1. Riegel's Handbook of Industrial Chemistry, Seventh Edition, J. A. Kent, ed. Van Nostrand Reinhold Co., New York, New York, 1974. pp. 551-569.

2. Handbook of Chemistry and Physics, 49th Edition, R. C. Weast, ed. The Chemical Rubber Co., Cleveland, Ohio, 1968. p. B-187.

3. Stowasser, W. F. Phosphate-1977. Publication No. MCP-2, U.S. Department of the Interior, Bureau of Mines, Washington, D.C., May 1977. 18 pp.

4. Fullam, H. T., and B. P. Faulkner. Inorganic Fertilizer and Phosphate Mining Industries--Water Pollution and Control (PB 206 154). Grant 12020 FPD, U.S. Environmental Protection Agency, Cincinnati, Ohio, September 1971. 225 pp.

5. Rawlings, G. D., and R. B. Reznik. Source Assessment: Fertilizer Mixing Plants. EPA-600/2-76-032c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 187 pp.

6. Inorganic Chemicals 1976. M28A(76)-14, U.S. Department of Commerce, Washington, D.C., August 1977. 30 pp.

7. Hargett, N. World Fertilizer Capacity-Computer Printout. Tennessee Valley Authority, Muscle Shoals, Alabama, 1976. 20 pp.

8. TVA Plans Early Closure of Furnaces; Cities Switch to Wet-Process Phosphoric. Chemical Marketing Reporter, 209(3), 1976.

9. Inorganic Fertilizer Materials and Related Products. M28B(75)-13, U.S. Department of Commerce, Washington, D.C., December 1976. 6 pp.

10. Harre, E. A., M. N. Goodson, and J. D. Bridges. Fertilizer Trends 1976. Bulletin Y-111, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama, March 1977. 45 pp.

11. Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants. EPA-450/2-77-005 (PB 265 062), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977. 277 pp.

12. Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture. AP-57 (PB 192 222), U.S. Department of Health, Education, and Welfare, Raleigh, North Carolina, April 1970. 86 pp.

13. Lowenheim, F. A. Phosphorus Compounds, Inorganic. In: Encyclopedia of Industrial Chemical Analysis, Volume 17, F. D. Snell and L. S. Ettre, eds. John Wiley & Sons, Inc., New York, New York, 1973. pp. 142-144.

14. Guimond, R. J., and S. T. Windham. Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes. ORP/CSD-75-3, U.S. Environmental Protection Agency, Washington, D.C., August 1975. 30 pp.

15. Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. 1159 pp.

16. Heller, A. N., S. T. Cuffe, and D. R. Goodwin. Inorganic Chemical Industry. In: Air Pollution, Volume III: Sources of Air Pollution and Their Control, A. C. Stern, ed. Academic Press, New York, New York, 1968. pp. 221-231.

17. Martin, E. E. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Chemicals Segment of the Fertilizer Manufacturing Point Source Category. EPA-440/1-74-011-a (PB 238 652), U.S. Environmental Protection Agency, Washington, D.C., March 1974. 170 pp.

18. Caro, J. H. Characterization of Superphosphate. In: Superphosphate: Its History, Chemistry, and Manufacture. U.S. Department of Agriculture, Washington, D.C., December 1964. pp. 272-284.

19. Dahlgren, S. E. Chemistry of Wet-Process Phosphoric Acid Manufacture. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 91-154.

20. Evaluation of Emissions and Control Techniques for Reducing Fluoride Emissions from Gypsum Ponds in the Phosphoric Acid Industry. Contract 68-02-1330, Task 3, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1976. 218 pp.

21. Slack, A. V. Chemistry and Technology of Fertilizers. John Wiley & Sons, Inc., New York, New York, 1967. pp. 69-97.

22. Lehr, J. R. Purification of Wet Process Acid. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 637-686.

23. Hill, W. L., H. L. Marshall, and K. D. Jacob. Composition of Crude Phosphoric Acid Prepared by Sulfuric Acid Process. Industrial and Engineering Chemistry, 24(9):1064-1068, 1932.

24. Lutz, W. A., and C. J. Pratt. Principles of Design and Operation. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 158-208.

25. Cleanup Pays Off for Fertilizer Plant. Environmental Science and Technology, 6(5):400-401, 1972.

26. Banford, C. R. IMC's New Plant Shows Off Latest H_3PO_4 Know-How. Chemical Engineering, 70(11):100-102, 1963.

27. Legal, C. C., and O. D. Myrick, Jr. History and Status of Phosphoric Acid. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 1-89.

28. Huffstutler, K. K. Pollution Problems in Phosphoric Acid Production. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 727-739.

29. Muehlberg, P. E., J. T. Reding, and B. P. Shepherd. Draft Report: The Phosphate Rock and Basic Fertilizer Materials Industry. Contract 68-02-1329, Task 8, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1976. 205 pp.

30. Personal communication with Ed Harre, Tennessee Valley Authority, Muscle Shoals, Alabama, 14 April 1977.

31. Background Information for Standards of Performance: Phosphate Fertilizer Industry, Vol. 1--Proposed Standards. EPA-450/2-74-019a (PB 237 606), U.S. Environmental Protection Agency, Raleigh, North Carolina, October 1974. 140 pp.

32. Gartrell, F. E., and J. C. Barber. Pollution Control Interrelationships. Chemical Engineering Progress, 62(10):44-47, 1966.

33. Final Guideline Document: Control of Fluoride Emissions From Existing Phosphate Fertilizer Plants. EPA-450/2-77-005 (PB 265 062), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977. 277 pp.

34. David, M. L., J. M. Malk, and C. C. Jones. Economic Analysis of Effluent Guidelines Fertilizer Industry. EPA-230/2-74-010 (PB 241 315), U.S. Environmental Protection Agency, Washington, D.C., January 1974.

35. The Condensed Chemical Dictionary, Eighth Edition, G. G. Hawley, ed. Van Nostrand Reinhold Company, New York, New York, 1971. p. 54.

36. Chemistry and Technology of Fertilizers, V. Sauchelli, ed. Reinhold Publishing Corp., New York, New York, 1960. pp. 251-268.

37. Waggaman, W. H. Phosphoric Acid, Phosphates, and Phosphatic Fertilizers, Second Edition. Reinhold Publishing Corp., New York, New York, 1952. pp. 308-344.

38. Himmelblau, D. M. Basic Principles and Calculations in Chemical Engineering, Second Edition. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1967. pp. 449-454.

39. Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 9. John Wiley & Sons, Inc., New York, New York, 1966. pp. 46-132.

40. Slack, A. V. Fertilizer Developments and Trends. Noyes Development Corp., Park Ridge, New Jersey, 1968. pp. 77-274.

41. Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 15. John Wiley & Sons, Inc., New York, New York, 1968. p. 260.

42. Shreve, R. N. Chemical Process Industries, Third Edition. McGraw-Hill Book Company, New York, New York, 1967. pp. 274-277.

43. Chopey, N. P. Diammonium Phosphate: New Plant Ushers in Process Refinements. Chemical Engineering, 69(6):148-150, 1962.

44. Vandegrift, A. E., L. J. Shannon, E. W. Lawless, P. G. Gorman, E. E. Sallee, and M. Reichel. Particulate Pollutant System Study, Vol. III--Handbook of Emission Properties. APTD-0745 (PB 203 522), U.S. Environmental Protection Agency, Durham, North Carolina, 1971. pp. 313-335.

45. Hardison, L. C. Air Pollution Control Technology and Costs in Seven Selected Areas. EPA-450/3-73-010 (PB 231 757), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1973. pp. 11-192.

46. Achorn, F. P., and H. L. Balay. Systems for Controlling Dust in Fertilizer Plants. In: TVA Fertilizer Conference, Tennessee Valley Authority Bulletin Y-78, Muscle Shoals, Alabama, August 1974. pp. 55-62.

47. Phosphate Fertilizer Plants Final Guideline Document Availability. Federal Register, 42(40):12022-12023, 1977.

48. Hoffmeister, G. Quality Control in a Bulk Blending Plant. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 59-70.

49. Barber, J. C. Environmental Control in Bulk Blending Plants. 1. Control of Air Emissons. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 39-46.

50. Inorganic Fertilizer Materials and Related Products. M28B(75)-11, U.S. Department of Commerce, Washington, D.C., January 1976. 6 pp.

51. Inorganic Fertilizer Materials and Related Products. M28B(75)-12, U.S. Department of Commerce, Washington, D.C., February 1976. 6 pp.

52. Inorganic Fertilizer Materials and Related Products. M28(76)-1, U.S. Department of Commerce, Washington, D.C., March 1976. 6 pp.

53. Inorganic Fertilizer Materials and Related Products. M28(76)-2, U.S. Department of Commerce, Washington, D.C., April 1976. 6 pp.

54. Inorganic Fertilizer Materials and Related Products. M28(76)-3, U.S. Department of Commerce, Washington, D.C., May 1976. 6 pp.

55. Inorganic Fertilizer Materials and Related Products. M28(76)-4, U.S. Department of Commerce, Washington, D.C., June 1976. 6 pp.

56. Inorganic Fertilizer Materials and Related Products. M28(76)-5, U.S. Department of Commerce, Washington, D.C., July 1976. 6 pp.

57. Inorganic Fertilizer Materials and Related Products. M28(76)-6, U.S. Department of Commerce, Washington, D.C., August 1976. 6 pp.

58. Inorganic Fertilizer Materials and Related Products. M28(76)-7, U.S. Department of Commerce, Washington, D.C., September 1976. 6 pp.

59. Inorganic Fertilizer Materials and Related Products. M28(76)-8, U.S. Department of Commerce, Washington, D.C., October 1976. 6 pp.

60. Inorganic Fertilizer Materials and Related Products. M28(76)-9, U.S. Department of Commerce, Washington, D.C., November 1976. 6 pp.

61. Inorganic Fertilizer Materials and Related Products. M28(76)-10, U.S. Department of Commerce, Washington, D.C., December 1976. 6 pp.

62. King, W. R., and J. K. Ferrell. Fluoride Emissions from Phosphoric Acid Plant Gypsum Ponds. EPA-650/2-74-021, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1974. 329 pp.

63. English, M. Fluorine Recovery from Phosphatic Fertilizer Manufacture. Chemical Process Engineering, 48(12):43-47, 1967.

64. Bowers, Q. D. Disposal as Waste Material - U.S. Practice. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 505-510.

65. Huffstutler, K. K., and W. E. Starnes. Sources and Quantities of Fluorides Evolved from the Manufacture of Fertilizer and Related Products. Journal of the Air Pollution Control Association, 11(12):682-684, 1966.

66. Preliminary Report: Remote Monitoring of Fluoride Emission from Gypsum Ponds. EPA-69/01-4145, Task 10, U.S. Environmental Protection Agency, Washington, D.C., November 1977. 35 pp.

67. Volk, W. Applied Statistics for Engineers, Second Edition. McGraw-Hill Book Co., New York, New York, 1969. 110 pp.

68. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1969. 62 pp.

69. Reznik, R. B. Source Assessment: Flat Glass Manufacturing Plants. EPA-600/2-76-032b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976. 147 pp.

70. TLV® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

71. National Emissions Data System Point Source Listing. SCC 3-01-030-01, 3-01-030-02, 3-01-030-99, 1976. 190 pp.

72. 1972 National Emissions Report; National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS). EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

73. Eimutis, E. C., and R. P. Quill. State-by-State Listing of Source Types that Exceed the Third Decision Criterion, Special Project Report. Contract 68-02-1874, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 7, 1975. pp. 1-3.

74. Seinfeld, J. H. Air Pollution: Physical and Chemical Fundamentals. McGraw-Hill Book Co., New York, New York, 1975. 523 pp.

75. Environmental Engineers' Handbook, Volume 2, Air Pollution, B. G. Liptak, ed. Chilton Book Co., Radnor, Pennsylvania, 1974. 1340 pp.

76. Specht, R. C., and R. R. Calaceto. Gaseous Fluoride Emissions from Stationary Sources. Chemical Engineering Progress, 63(5):78-84, 1967.

77. Frazier, A. W., E. F. Dillard, and J. R. Lehr. Chemical Behavior of Fluorine in the Production of Wet Process Phosphoric Acid. Presented at the American Chemical Society Annual Meeting, Chicago, Illinois, August 24-29, 1975. 16 pp.

78. Environmental Considerations of Selected Energy Conserving Manufacturing Process Options, Vol. 13, Phosphorus/Phosphoric Acid Industry Report. EPA-600/7-76-034m (PB 264 279), U.S. Environmental Protection Agency, Cincinnati, Ohio, December 1976. 96 pp.

79. 40 CFR 418, Fertilizer Manufacturing Point Source Category, Subpart A - Phosphate Subcategory. Federal Register, 41(98):20582-20585, 1976.

80. Quality Criteria for Water. EPA-440/9-76-023, U.S. Environmental Protection Agency, Washington, D.C., 1976. pp. 16-21.

81. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. EPA-600/8-77-005, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1977. 73 pp.

82. Eimutis, E. C., J. L. Delaney, T. J. Hoogheem, S. R. Archer, J. C. Ochsner, W. R. McCurley, T. W. Hughes, and R. P. Quill. Source Assessment: Prioritization of Stationary Water Pollution Sources. EPA-600/2-77-107p, U.S. Environmental Protection Agency, Washington, D.C., December 1977. 119 pp.

83. Water Resources Data for Florida, Water Year 1975. Volume 3 - West-Central Florida Surface Water, Ground Water, Quality of Water. USGS-WRD-FL-75-3 (PB 259 493), U.S. Department of Commerce, Tallahassee, Florida, July 1976. 1249 pp.

84. Water Resources Data for Kentucky, Water Year 1975. USGS-WDR-KY-75-1 (PB 251 853), U.S. Department of Commerce, Louisville, Kentucky, January 1976. 348 pp.

85. Personal communication with John Sweeney, U.S. Bureau of Mines, Tallahassee, Florida, 26 September 1977.

86. Murakami, K. By-product Recovery, As Raw Material for Plaster and Cement - Japanese Practice. In: Phosphoric Acid, Volume I, A. V. Slack, ed. Marcel Dekker, Inc., New York, New York, 1968. pp. 519-523.

87. Phillips, A. B. New Products for the Future. In: TVA Fertilizer Bulk Blending Conference, Tennessee Valley Authority Bulletin Y-62, Muscle Shoals, Alabama, August 1973. pp. 23-27.

88. Background Information for Standards of Performance: Phosphate Fertilizer Industry, Vol. 2--Test Data Summary. EPA-450/2-74-019b (PB 237 607), U.S. Environmental Protection Agency, Raleigh, North Carolina, October 1974. 63 pp.

89. Run of the Pile Triple Superphosphate. Contract 68-02-0232, Test Report 73-FRT-10, U.S. Environmental Protection Agency, Washington, D.C., September 1972. 45 pp.

90. Normal Superphosphate Plant. Contract 68-02-0232, Test Report 73-FRT-15, U.S. Environmental Protection Agency, Washington, D.C., June 1973. 32 pp.

91. Granular Triple Superphosphate Storage. Contract 68-02-0232, Test Report 72-CI-30B, U.S. Environmental Protection Agency, Washington, D.C., June 1972. 32 pp.

92. Sanders, L. Monitoring and Control of Gaseous and Particulate Emissions from Fertilizer Complex. Presented at the 69th Annual Meeting of the Air Pollution Control Association (Paper No. 76-56), Portland, Oregon, June 27-July 1, 1976. 14 pp.

93. Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^{\epsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

APPENDIX A

PHOSPHATE FERTILIZER PLANTS IN THE UNITED STATES IN 1975 OR 1976

Table A-1 lists 1975 ammonium phosphate production figures. Tables A-2 through A-6 describe the phosphate fertilizer plants operating in the United States in 1975 or 1976, of which there were 36 producing WPPA, Table A-2 (7); 9 producing superphosphoric acid, Table A-3 (7); 66 producing NSP, Table A-4 (7); 16 producing TSP, Table A-5 (10); and 48 producing ammonium phosphate, Table A-6 (7, 10, 11). Plant lists were modified by MRC based on communications with industry representatives. The company name and location of each plant are provided in the tables, along with plant production capacity and population density of the county where the plant is located.

In order to have a consistent industry characterization, a conversion factor from P_2O_5 to product was needed for ammonium phosphate production. Using U.S. Department of Commerce data for the industry in 1975 (Table A-1), a conversion of

$$\text{Mass product} = \text{Mass } P_2O_5(2.49) \qquad \text{(A-1)}$$

was generated and used.

Pure DAP has a 4.0:1.0 mole ratio of $N:P_2O_5$, and MAP has a ratio of 2.0:1.0. According to the U.S. Department of Commerce, the ratio for DAP in 1975 was 4.25:1.0; for other phosphates it was 4.47:1.0. This suggests that more nitrogen than phosphorus was being tied up by impurities; i.e., nitrogen was reacting with materials other than phosphoric acid, forming either soluble or insoluble salts. The nutrient analysis for U.S. Department of Commerce DAP was 18-44-0, very close to the most common WPPA DAP product (18-46-0). The analysis for other phosphates was 12-27-0. Along with the high $N:P_2O_5$ ratio, this suggests the presence of large quantities of ammonium salts other than phosphates; e.g., ammonium sulfate. The analysis could result from a mixture of common MAP fertilizers: 11-48-0, 11-55-0, 13-52-0, and 16-20-0.

TABLE A-1. 1975 PRODUCTION OF AMMONIUM PHOSPHATES (50-61)

Month	Production, metric tons								
	Diammonium phosphate			Other ammonium phosphates			Total ammonium phosphates		
	P_2O_5	N	Gross	P_2O_5	N	Gross	P_2O_5	N	Gross
January	156,407	63,829	320,894	32,537	16,083	138,223	188,944	79,912	459,117
February	160,105	65,399	362,044	39,691	17,340	147,550	199,797	82,740	509,594
March	168,923	76,236	378,444	39,057	19,869	165,781	207,980	96,105	544,225
April	180,179	90,631	392,222	36,410	15,771	142,098	216,589	106,402	534,320
May	207,453	84,717	455,907	35,091	17,613	145,515	242,544	102,330	601,421
June	197,970	81,642	461,246	32,999	14,101	121,874	230,969	95,742	583,120
July	174,783	71,743	430,664	39,672	16,554	139,626	214,456	88,297	570,290
August	193,985	79,058	464,931	39,122	16,866	127,679	233,107	95,924	592,610
September	215,897	87,497	507,117	32,172	14,982	107,617	248,068	102,479	614,734
October	232,775	95,105	537,130	37,770	15,083	113,214	270,545	110,189	650,344
November	210,999	86,361	469,638	38,324	14,928	128,903	249,323	101,289	598,541
December	211,479	85,444	473,742	37,031	14,558	129,803	248,510	100,002	603,545
Total	2,310,955	967,662	5,253,979	439,876	193,749	1,607,883	2,750,831	1,161,411	6,861,862

TABLE A-2. WPPA PLANTS IN THE UNITED STATES IN 1975 (7)

Company	Location	Design production capacity, metric tons P_2O_5/day (short tons P_2O_5/day)	County population density, persons/km^2
Allied Chemical Corp., Union Texas Petroleum Division	Geismar, LA	454(500)	46.7
Beker Industries Corp.	Conda, ID	690(760)[a]	1.4
	Marseilles, IL	290(320)[a]	36.9
	Taft, LA	600(660)[a]	37.1
Borden, Inc., Smith-Douglas Division	Piney Point, FL	454(500)	49.0
	Streator, IL	55(60)[a]	36.9
C F Industries, Inc.	Bartow, FL	1,900(2,100)	46.1
	Plant City, FL	725(800)	180.1
		1,090(1,200)	
Engelhard Minerals and Chemicals Corp.	Nichols, FL	363(400)	46.1
Farmland Industries, Inc.	Greenbay, FL	1,270(1,400)	46.1
First Mississippi Corp.	Ft. Madison, IA	658(725)	30.7
Freeport Minerals Co.	Uncle Sam, LA	2,087(2,300)	29.6
The Gardinier Companies:			
Gardinier, Inc.	Tampa, FL	1,360(1,500)	466.8
Gardinier Big River, Inc.	Helena, AR	136(150)	22.3
W. R. Grace and Co., Agricultural Products Group	Bartow, FL	907(1,000)	46.1
International Minerals and Chemicals Corp.	New Wales, FL	1,655(1,824)	46.1
Mississippi Chemical Corp.	Pascagoula, MS	590(650)	44.8
Mobil Oil Corp., Agricultural Chemicals Division	Depue, IL	354(390)	16.9
North Idaho Phosphate Co.	Kellogg, ID	82(90)	2.9

(continued)

TABLE A-2 (continued)

Company	Location	Design production capacity, metric tons P_2O_5/day (short tons P_2O_5/day)	County population density, persons/km^2
Occidental Petroleum Corp., Occidental Chemical Co.	Lanthrop, CA	110(120)[a]	77.7
	White Springs, FL	635(700) 662(730) 345(380)	5.8
Olin Corp., Agricultural Chemicals Division	Pasadena, TX	658(725)	385.9
	Joliet, IL	417(460)	274.9
Pennzoil Co.	Hanford, CA	55(60)[a]	17.8
Royster Co.	Mulberry, FL	381(420)	46.1
J. R. Simplot Co., Minerals and Chemicals Division	Pocatello, ID	522(575) 290(320)	17.5
Stauffer Chemical Co., Fertilizer and Mining Division	Pasadena, TX	163(180)	385.9
	Salt Lake City, UT	181(200)	235.7
Texasgulf, Inc., Agricultural Division	Aurora, NC	953(1,050) 476(525) 476(525)	16.1
Union Oil Co. of California	Nichols, CA	23(25)	49.0
United States Steel Corp., USS Agri-Chemicals Division	Bartow, FL	272(300)	46.1
	Ft. Meade, FL	535(590)	46.1
Valley Nitrogen Producers, Inc.	Bakersfield, CA	18(20)	15.4
	Helm, CA	127(140) 227(250)	4.9
The Williams Companies, Agrico Chemical Co.	Donaldsville, LA	1,143(1,260)	46.7
	South Pierce, FL	771(850)	46.1

[a] MRC estimate.

TABLE A-3. SUPERPHOSPHORIC ACID PLANTS IN THE UNITED STATES IN 1975 WHICH DERIVE THEIR PRODUCT FROM WPPA (7)

Company	Location	Design production capacity, metric tons P_2O_5/day (short tons P_2O_5/day)	Type of concentration	County population density, persons/km^2
Allied Chemical Corp., Union Texas Petroleum Division	Geismar, LA	417(460)	Submerged combustion	46.7
Farmland Industries, Inc.	Greenbay, FL	454(500)	Vacuum evaporation	46.1
International Minerals and Chemicals	Bonnie, FL	460(508)	Vacuum evaporation	46.1
North Idaho Phosphate Co.	Kellogg, ID	36 (40)	Vacuum evaporation	2.9
Occidental Petroleum Corp. Occidental Chemical Co.	White Springs, FL	227(250) 118(130)	Submerged combustion	5.8
J. R. Simplot Co., Minerals and Chemicals Division	Pocatello, ID	104(115) 77(85)	Vacuum evaporation	17.5
Stauffer Chemical Co., Fertilizer and Mining Division	Pasadena, TX	72(79)	Vacuum evaporation	385.9
	Salt Lake City, UT	113(125)	Vacuum evaporation	235.7
Texasgulf Inc., Agricultural Division	Aurora, NC	275(303) 275(303) 269(297)	Vacuum evaporation	16.1

TABLE A-4. NSP PLANTS IN THE UNITED STATES IN 1976 (7)

Plant name	Location	Production capacity, metric tons P_2O_5/yr	County population density, persons/km^2
American Plant Food Corp.	Fort Worth, TX	[a]	316.3
	Houston, TX	9,070	385.8
Borden Inc., Chemical Division	Norfolk, VA	27,200	1,991.6
	Russelville, KY	6,000	14.7
	Streator, IL	32,700	36.9
Centrala Farmers Coop., Inc.	Forkland, AL	5,440	6.2
Columbia Nitrogen Corp.	Moultrie, GA	11,800	21.6
Farmers Fertilizer	Texarkana, TX	9,070	19.9
Gardinier, Inc.	Tampa, FL	6,350	180.1
Georgia Fertilizer	Valdosta, GA[b]	17,200	40.7
Gilchrist Plant Food	Morris, IL	3,630	23.0
Gold Kist, Inc.	Clyo, GA	7,260	10.7
	Cordele, GA	10,900	23.4
W. R. Grace and Co.	Charleston, SC	14,500	94.6
	Joplin, MO	13,600	47.3
	Nashville, TN	13,600	401.8
Indiana Farm Bureau Coop. Association, Inc.	Indianapolis, IN[b]	12,700	757.5
International Minerals and Chemical Corp.	Americus, GA	8,160	20.9
	Augusta, GA	[a]	192.2
	Chicago Heights, IL[b]	10,900	2,195.6
	Florence, AL	12,700	39.0
	Fort Worth, TX[b]	12,700	316.3
	Hartsville, SC	[a]	36.9
	Spartanburg, SC	10,900	78.8
	Winston Salem, NC	[a]	189.2
Kaiser Aluminum and Chemical Corp., Agriculture Chemicals Division	Acme, NC[b]	20,000	18.7
Kerr-McGee Corp.	Baltimore, MD	9,980	397.4
	Cottondale, FL	11,800	13.8
	Jacksonville, FL[b]	17,200	258.7
	Philadelphia, PA	16,300	5,858.7
Layco	Lakeland, FL	[a]	46.1
Lone Star Co., NIPAK, Inc., Subsidiary	Nacagodoches, TX	4,340	14.9
Mineral Fertilizer Co.	Midvale, UT	2,720	235.7
Occidental Petroleum Corp., Occidental Chemical Co., Subsidiary	Ashkum, IL	6,350	11.2
	White Springs, FL	6,350	5.8
Ohio Valley Fertilizer	London, KY	16,300	23.3
Pelham Phosphate Co.	Pelham, GA	8,160	14.1
Richmond Guano Co.	Richmond, VA	10,900	2,519.6
Royster Co.	Athens, GA	3,630	196.5
	Chesapeake, VA	9,980	99.8
	Jackson, MS	5,440	92.3
Southern States Phosphate and Fertilizer Co.	Savannah, GA	24,500	158.7
Stauffer Chemical Co.	Tacoma, WA	9,980	93.3
Swift and Co., Swift Chemical Co., Division	Bartow, FL	13,600	46.1
	Birmingham, AL[b]	11,800	221.1
	Charleston, SC[b]	6,350	94.6
	Dothan, AL	12,700	37.0
	Norfolk, VA[b]	9,070	1,991.6
	Savannah, GA	6,350	158.7
	Wilmington, NC	9,070	160.6
Texaco, Inc.	Omaha, NE[b]	10,900	446.1
U.S. Steel Corp., USS Agri-Chemicals Division	Albany, GA	13,000	105.7
	Columbus, GA[b]	6,350	2,195.6
	Nashville, TN	14,000	401.8
	Navassa, NC	15,000	167.9
Valley Nitrogen Producers, Inc.	Bakersfield, CA	[a]	15.4
Weaver Fertilizer Co., Inc.	Norfolk, VA	13,600	1,991.6
The Williams Companies, Agrico Chemical Co., Inc., Subsidiary	Buffalo, NY[b]	9,980	402.5
	Cairo, OH[b]	9,980	104.3
	Charleston, SC[b]	8,160	94.6
	Fulton, IL[b]	21,800	34.7
	Greensboro, NC[b]	5,440	167.9
	Pensacola, FL[b]	6,350	116.7
	Pierce, FL[b]	8,160	46.1
	Saginaw, MI[b]	10,900	103.3
	Walnut Ridge, AK[b]	5,440	10.6

[a] Plant production capacity not available.

[b] Plants closing during calendar year 1976 or during the first half of 1977.

TABLE A-5. TSP PLANTS IN THE UNITED STATES IN 1976 (10)

Plant name	Location	Production capacity,[a] metric tons P_2O_5/yr		County population density, persons/km^2
		GTSP	ROP-TSP	
Borden Inc., Chemical Division	Piney Point, FL	29,900	0	49.0
CF Industries, Inc.	Plant City, FL	190,000	150,000	180.1
Engelhard M. and C.	Nichols, FL	0	117,000	46.1
Farmland Industries, Inc.	Pierce, FL	79,000	0	46.1
Gardinier, Inc.	Tampa, FL	190,000	150,000	180.1
W. R. Grace and Co.	Bartow, FL	163,000	128,000	46.1
	Joplin, MO[b]	0	40,800	47.3
International Minerals and Chemical Corp.	Bonnie, FL	125,000	0	46.1
Mississippi Chemical Corp.	Pascagoula, MS	114,000	0	44.8
Occidental Petroleum Corp., Occidental Chemical Co., Subsidiary	White Springs, FL	70,800	0	5.8
Royster Co.	Mulberry, FL	0	88,000	46.1
J. R. Simplot Co.	Pocatello, ID	35,000	27,600	17.5
Stauffer Chemical Co.	Garfield, UT	20,800	16,400	235.7
Texasgulf, Inc.	Lee Creek, NC	130,000	102,000	16.1
U.S. Steel Corp., USS Agri-Chemicals, Division	Fort Meade, FL	110,000	0	46.1
The Williams Companies, Agrico Chemical Co., Subsidiary	Pierce, FL[b]	140,000	110,000	46.1

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[a] For those plants which produced both GTSP and ROP-TSP, a product distribution of 56% GTSP and 44% ROP-TSP was assumed, based on total share of the market.

[b] Plants closing during calendar year 1976 or during the first half of 1977.

TABLE A-6. AMMONIUM PHOSPHATE PLANTS IN THE UNITED STATES IN 1975 (7, 10, 11)

Company	Location	Production capacity: 10^3 metric tons P_2O_5/yr	Production capacity: 10^3 metric tons product/yr	County population density, persons/km²
Allied Chemical Corp.	Geismar, LA	123	306	46.7
Beker Industries	Conda, ID	146	365	1.4
	Taft, LA	182	454	37.1
Borden Chemical Co.	Piney Point, FL	77	193	49.0
Brewster Phosphates	Luling, LA	136	340	96.2
	Geismar, LA	45	113	46.7
CF Industries, Inc.	Bonnie, FL	577	1,440	46.1
	Plant City, FL	250	624	180.1
Conserv, Inc.	Nichols, FL	109	272	46.1
Farmland Industries, Inc.	Pierce, FL	164	408	46.1
	Joplin, MO	84	209	47.3
First Mississippi Corp.	Fort Madison, IA	155	386	30.7
Ford Motor Co.	Dearborn, MI	9	23	1,686.3
Gardinier, Inc.	Tampa, FL	227	567	180.1
	Helena, AR	45	113	22.3
W. R. Grace & Co.	Bartow, FL	95	238	46.1
Gulf Resources	Kellogg, ID	19	48	2.9
IMC Chemicals Corp.	Bartow, FL	227	567	46.1
Kaiser Aluminum & Chemical	Wendover, UT	14	34	1.2
Kaiser Steel	Fontana, CA	14	34	12.9
Mississippi Chemical Corp.	Pascagoula, MS	139	347	44.8
Mobil Chemical Co.	Depue, IL	114	283	13.0
Monsanto Industrial Chemicals Co.	Trenton, MI[a]	16	41	1,686.3
Nipak, Inc.	Kerens, TX	30	75	10.8
North Idaho Phosphate Co.	Kellogg, ID[a]	24	59	2.9
Northwest Coop Mills	Pine Bend, MN	63	156	92.9
Occidental Petroleum Corp., Occidental Chemical Co., Subsidiary	White Springs, FL	275	687	5.8
	Lathrop, CA	16	41	77.7
	Plainview, TX[a]	9	23	13.2
Olin Corp.	Pasadena, TX	209	522	385.9
Pennzoil Co.	Hanford, CA	–[b]	–[b]	17.8
Phosphate Chemicals	Pasadena, TX	45	113	385.9
Royster Co.	Mulberry, FL	45	113	46.1
J. R. Simplot Co.	Pocatello, ID	73	181	17.5
Standard Oil Co. of California	Fort Madison, IA[a]	73	181	30.7
	Kennewick, WA[a]	27	68	14.9
	Richmond, CA[a]	36	91	151.8
Stauffer Chemical	Garfield, UT	51	127	235.7
Tennessee Valley Authority	Muscle Shoals, AL	18	45	31.8
Texas Gulf, Inc.	Lee Creek, NC	92	229	16.1
Union Oil Co. of California	Nichols, CA[a]	20	50	49.0
USS Agri-Chemicals	Cherokee, AL	68	170	31.8
	Bartow, FL	13	32	46.1
Valley Nitrogen Producers	Helm, CA	32	79	26.3
	Fresno, CA	–[b]	–[b]	26.3
	Chandler, AZ	11	27	4.9
Williams Companies, Agrico Chemical Co., Subsidiary	Pierce, FL	42	104	46.1
	Donaldsonville, LA	687	1,714	46.7
U.S. total		4,926	12,292	

[a] 1973 Gross capacities reported in Reference 10 assumed unchanged for 1975.

[b] Capacity information unavailable.

APPENDIX B

EMISSIONS DATA

The following tables present stack test data from individual plants used to calculate emission factors.

TABLE B-1. WPPA PLANT SOURCE TEST DATA FOR ROCK UNLOADING[a]

Plant	Test production, metric tons P_2O_5/hr	Controlled particulate emission factor, g/kg P_2O_5	Stack height, m
A	63.3	0.18	14
B	12.7	0.26	b
C	23.8	0.017	10
Averages	32.3	0.15 ± 250%	12

[a] Emissions data on file at the Florida Department of Environmental Regulation in Winter Haven.

[b] No data available.

TABLE B-2. WPPA PLANT SOURCE TEST DATA FOR ROCK TRANSFER AND CHARGING TO REACTOR[a]

Plant	Test production, metric tons P_2O_5/hr	Controlled particulate emission factor, g/kg P_2O_5	Stack height, m
A	63.3	0.006	17
B	50.6	0.012	b
D	18.5	0.062	18
E	22.8	0.10	27
Averages	38.8	0.045 ± 180%	21

[a] Emissions data on file at the Florida Department of Environmental Regulation in Winter Haven.

[b] No data available.

TABLE B-3. WPPA PLANT SOURCE TEST DATA FOR WET SCRUBBER SYSTEM[a,b]

Plant	Test production, metric tons P_2O_5/hr	Controlled emission factors, g/kg P_2O_5				Recovers byproduct of fluorine	Controlled fluorine emission factors, g/kg P_2O_5		Stack height, m
		Total fluorine	Particulate	P_2O_5	SO_x		With recovery	Without recovery	
A	24.2	0.012		0.045		No	NA[c]	0.012	37
	23.9	0.007		0.040		No	NA	0.007	
	23.7	0.011		0.030		No	NA	0.011	
B	34.0	0.0033				No	NA	0.0033	
	41.6	0.0042				No	NA	0.0042	
D	14.4	0.0083	0.036		0.0077	No	NA	0.0083	17
F	29.3	0.0033	0.0011			Yes	0.0033	NA	21
	19.4	0.0055				Yes	0.0055	NA	
G	39.4	0.0039	0.053			Yes	0.0039	NA	28
H	6.0	0.035	0.17			No	NA	0.035	37
I	18.4	0.011				Yes	0.011	NA	
	18.4	0.0025				Yes	0.0025	NA	
J	8.5	0.012				No	NA	0.012	
	19.3	0.012				No	NA	0.012	
K	50.6	0.009	0.0038			Yes	0.009	NA	31
L	15.3	0.011				NA	NA	NA	
M	37.8	0.010				NA	NA	NA	
N					0.058	NA	NA	NA	
O					0.029	NA	NA	NA	
Averages	24.9	0.010	0.054	0.038	0.032		0.0059	0.012	29

[a] Data for plants A through K from plant test data on file at the Florida Department of Environmental Regulation in Winter Haven. Data for plants L and M from material balances shown earlier in Table 19. SO_x emission factors for plants N and O taken from data available in Reference 12.

[b] Blanks indicate no data available.

[c] Not applicable.

TABLE B-4. SUPERPHOSPHORIC ACID PLANT SOURCE TEST DATA FOR WET SCRUBBER SYSTEM[a]

Plant	Test production, metric tons P_2O_5/hr	Controlled emission factor, g/kg P_2O_5		Stack height, m
		Total fluorine	Particulate	
AA	9.0	b	0.011 to 0.055	27
BB	12.5	0.0036		21
CC	20.44	0.011		15
Averages	14.0	0.0073		21

[a] Emissions data on file at the Florida Depratment of Environmental Regulation in Winter Haven.

[b] Blanks indicate no data available.

TABLE B-5. PLANT SOURCE TEST DATA FOR ROP-TSP MANUFACTURE

Plant	Production rate	Source of emissions	Reported controlled emission factor		Controlled emission factor, g/kg P_2O_5		Date of analysis	Reference
			Fluoride	Particulate	Fluoride	Particulate		
A	14.2 tons	Mixer, den, storage	0.321 lb/ton P_2O_5		0.161		2/72	88
	14.5 tons	Mixer, den, storage	0.228 lb/ton P_2O_5		0.114		2/72	88
	15.1 tons	Mixer, den, storage	0.035 lb/ton P_2O_5		0.018		3/72	88
	16.2 tons	Mixer, den, storage	0.181 lb/ton P_2O_5		0.091		9/72	88
	16.1 tons	Mixer, den, storage	0.304 lb/ton P_2O_5		0.152		9/72	88
	16.3 tons	Mixer, den, storage	0.147 lb/ton P_2O_5		0.074		9/72	88
	–[a]	Mixer, den, storage	0.074 to 0.345 lb/ton P_2O_5[a]		0.037 to 0.173[a]		1972	88
	6.46 tons	Mixer, den, storage	0.319 lb/ton P_2O_5		0.160		1975	–[b]
B	33.6 tons	Mixer, den, storage	0.125 lb/ton P_2O_5		0.063		9/72	89
	34.8 tons	Mixer, den, storage	0.126 lb/ton P_2O_5		0.063		9/72	89
	35.8 tons	Mixer, den, storage	0.125 lb/ton P_2O_5		0.063		9/72	89
	–[c]	Mixer, den, storage	0.022 to 0.230 lb/ton P_2O_5[c]		0.011 to 0.115[c]		1972	89
C[d,e]	37.6 metric tons TSP/hr	Mixer, den	13.9 lb/day	7.0 lb/hr	0.022	0.17	1974	–[b]
	38.2 metric tons TSP/hr	Mixer, den	17.1 lb/day	7.2 lb/hr	0.026	0.18	1974	–[b]
	40.4 metric tons TSP/hr	Mixer, den	0.66 lb/hr	2.0 lb/hr	0.015	0.046	1975-76	–[b]
	20.1 metric tons P_2O_5/hr	Mixer, den	0.45 lb/hr	2.1 lb/hr	0.01	0.048	2/76	–[b]
	20.3 metric tons P_2O_5/hr	Mixer, den	0.25 lb/hr	2.6 lb/hr	0.005	0.06	5/76	–[b]
	40.5 metric tons TSP/hr	Mixer, den	0.74 lb/hr	4.5 lb/hr	0.017	0.103	1975-76	–[b]
	20.1 metric tons P_2O_5/hr	Mixer, den	0.58 lb/hr	3.54 lb/hr	0.013	0.080	5/76	–[b]
	50.7 metric tons TSP/hr	Screening, milling and shipping	3.6 lb/day	4.4 lb/hr	0.0043	0.09	1974	–[b]
	54.4 metric tons TSP/hr	Mixer, den	0.37 lb/hr	2.2 lb/hr	0.007	0.038	1975-76	–[b]

[a] Range of 35 stack tests made by plant operator not included in developing average emission factor.

[b] Emissions data on file at the Florida Department of Environmental Regulation in Winter Haven.

[c] Range of 51 stack tests made by plant operator not included in developing average emission factor.

[d] Assuming 16 hr/day plant operation to convert from pounds per day to pounds per hour and 49% P_2O_5 content in ROP-TSP to convert from pounds TSP to pounds P_2O_5.

[e] Fluoride emission measurements for Plant C were not included in the statistical analysis due to the fact that a curing dryer is used in place of the curing building.

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(88) Background Information for Standards of Performance: Phosphate Fertilizer Industry, Vol. 2--Test Data Summary. EPA-450/2-74-019b (PB 237 607), U.S. Environmental Protection Agency, Raleigh, North Carolina, October 1974. 63 pp.

(89) Run of the Pile Triple Superphosphate. Contract 68-02-0232, Test Report 73-FRT-10, U.S. Environmental Protection Agency, Washington, D.C., September 1972. 45 pp.

TABLE B-6. PLANT SOURCE TEST DATA FOR NSP MANUFACTURE

Plant	Production rate	Source of emissions	Reported controlled emission factor		Controlled emission factor, g/kg P_2O_5		Date of analysis	Reference
			Fluoride	Particulate	Fluoride	Particulate		
A	2.89 metric tons P_2O_5/hr	Mixer, den	0.061 lb/ton P_2O_5		0.031		1974-75	[a]
	2.33 metric tons P_2O_5/hr	Mixer, den	0.03 lb/ton P_2O_5		0.015		3/76	[a]
	2.70 metric tons P_2O_5/hr	Mixer, den	0.03 lb/ton P_2O_5		0.015		3/76	[a]
		Curing building	0.4380 lb/hr		0.073[b] 2.43-uncontrolled[c]		8/74	[a]
		Curing building	0.6665 lb/hr		0.111[b] 3.70-uncontrolled[c]		1/75	[a]
		Curing building	0.101 lb/hr		0.017[b] 0.57-uncontrolled[c]		3/76	[a]
		Curing building	0.154 lb/hr		0.026[b] 0.85-uncontrolled[c]		3/76	[a]
B	18.1 metric tons NSP/hr	Mixer, den	0.141 lb/ton NSP[d]		0.353		6/73	90
	18.1 metric tons NSP/hr	Mixer, den	0.083 lb/ton NSP[d]		0.208		6/73	90
	18.1 metric tons NSP/hr	Mixer, den		0.205 lb/ton NSP[d]		0.52	6/73	90
	18.1 metric tons NSP/hr	Mixer, den		0.0986 lb/ton NSP[d]		0.247	6/73	90
	18.1 metric tons NSP/hr	Mixer, den		0.140 lb/ton NSP[d]		0.35	6/73	90
C	22.5 metric tons NSP/hr	Mixer, den	4.5 lb/day	1.5 lb/hr	0.0565[e]	0.15[e]	1974	[a]
	14.2 metric tons NSP/hr	Mixer, den	0.12 lb/hr	0.30 lb/hr	0.019[e]	0.048[e]	1975	[a]

[a] Emissions data on file at the Florida Department of Environmental Regulation. [b] Assuming average plant production rate of 3 tons P_2O_5/hr.

[c] Using reported scrubber control efficiency of 97% for fluoride removal. [d] Assuming a 20% P_2O_5 content in the NSP product.

[e] Assuming 8 hr/day operation and a 20% P_2O_5 content in the NSP.

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(90) Normal Superphosphate Plant. Contract 68-02-0232, Test Report 73-FRT-15, U.S. Environmental Protection Agency, Washington, D.C., June 1973. 32 pp.

TABLE B-7. PLANT SOURCE TEST DATA FOR GTSP MANUFACTURE

Plant	Production rate	Source of emissions	Reported controlled emission factor			Controlled emission factor, g/kg P_2O_5			Date of analysis	Reference
			Fluoride	SO_x as SO_2	Particulate	Fluo-ride	SO_x as SO_2	Partic-ulate		
A	31.4 metric tons P_2O_5/hr	Reactor, granulator cooler, dryer, screens	1.276 lb/hr	153.6 lb/hr[a]		0.02	2.22		5/76	b
	33.1 metric tons rock/hr	Rock feeder			0.3217 lb/hr			0.004[c]	5/76	b
	54.4 metric tons GTSP/hr	Shipping and curing building			3 lb/hr			0.055[c]		b
B	12.2 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.278 lb/ton P_2O_5			0.139			6/72	88
	13.8 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.174 lb/ton P_2O_5			0.087			6/72	88
	13.7 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.182 lb/ton P_2O_5			0.091			6/72	88
		Reactor, granulator, cooler, dryer, screens	0.28 lb/ton P_2O_5			0.14				91
		Reactor, granulator, cooler, dryer, screens	0.17 lb/ton P_2O_5			0.09				91
		Reactor, granulator, cooler, dryer, screens	0.18 lb/ton P_2O_5			0.09				91
	245 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	0.24 lb/ton P_2O_5			0.12			1975	b
	363 metric tons P_2O_5/day	Curing building	0.06 lb/ton P_2O_5			0.03			1975	b
	1,815 metric tons P_2O_5 stored	Curing building	0.0007 lb/hr P_2O_5			0.042[d]			9/72	91
	1,815 metric tons P_2O_5 stored	Curing building	0.0002 lb/hr ton P_2O_5 stored			0.012[d]			9/72	91
	1,815 metric tons P_2O_5 stored	Curing building	0.0005 lb/hr ton P_2O_5 stored			0.030[d]			9/72	91
	4,084 metric tons P_2O_5 stored	Curing building	0.00006 lb/hr ton P_2O_5 stored			0.008[d]			6/72	88
	4,085 metric tons P_2O_5 stored	Curing building	0.00005 lb/hr ton P_2O_5 stored			0.007[d]			6/72	88
	4,084 metric tons P_2O_5 stored	Curing building	0.00006 lb/hr ton P_2O_5 stored			0.008[d]			6/72	88
	3,525 metric tons P_2O_5 stored	Curing building	0.00015 lb/hr ton P_2O_5 stored			0.013[d]			5/72	88
C	277 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	0.537 lb/ton P_2O_5			0.269			6/76	b
D	274 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	149 lb/day			0.25			1976	b
	428 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	183 lb/day			0.20			1975	b
	386 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	182 lb/day			0.22			1974	b
	356 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	178 lb/day			0.23			1973	b
	420 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	179 lb/day			0.20			1972	b
	443 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	169 lb/day			0.18			1971	b
	395 metric tons P_2O_5/day	Reactor, granulator, cooler, dryer, screens	206 lb/day			0.24			1970	b
	128,123 metric tons rock/yr	Rock feeder			0.04 lb/ton rock			0.019	7/76	b
	130,137 metric tons GTSP/yr	Shipping and curing building			0.01 lb/ton GTSP			0.44[e]	7/76	b

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See footnotes at end of table, p. 172.

(continued)

TABLE B-7 (continued)

Plant	Production rate	Source of emissions	Reported controlled emission factor			Controlled emission factor, g/kg P_2O_5			Date of analysis	Reference
			Fluoride	SO_x as SO_2	Particulate	Fluoride	SO_x as SO_2	Particulate		
E	52 metric tons GTSP/hr	Reactor, granulator, cooler, dryer, screens	0.05 lb/ton P_2O_5	1,866 lb/day[a]	0.41 lb/ton[f] P_2O_5	0.03[f]	1.5	0.21	1974-75	b
F	18 metric tons rock/hr	Rock feeder			0.06 lb/ton rock			0.028[c]	10/75	b
	45 metric tons rock/hr	Rock unloading			0.14 lb/ton rock			0.07[c]	10/75	b
G	21.1 metric tons P_2O_5/hr	Reactor, granulator, dryer, screens	0.026 lb/ton P_2O_5		0	0.013		0	1/76	b
	21.1 metric tons P_2O_5/hr	Reactor, granulator, dryer, screens	0.028 lb/ton P_2O_5		0	0.014		0	1/76	b
	21.1 metric tons P_2O_5/hr	Reactor, granulator, dryer, screens	0.026 lb/ton P_2O_5		0	0.013		0	1/76	b
	21.1 metric tons P_2O_5/hr	Rock unloading			5 lb/hr			0.11	1/76	b
	704 metric tons P_2O_5/day	Curing building	0.19 lb/hr		0	0.003		0	1/76	b
	704 metric tons P_2O_5/day	Curing building	0.188 lb/hr		0	0.003		0	1/76	b
	704 metric tons P_2O_5/day	Curing building	0.37 lb/hr		0	0.006		0	1/76	b
M	10.9 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.06 lb/ton P_2O_5			0.03			9/72	88
	10.9 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.18 lb/ton P_2O_5			0.09			1/72	88
	10.9 metric tons P_2O_5/hr	Reactor, granulator, cooler, dryer, screens	0.12 lb/ton P_2O_5			0.06			1/72	88
	1,316 metric tons P_2O_5 stored	Reactor, granulator, cooler, dryer, screens	0.00042 lb/hr ton			0.033[g]				88
	1,316 metric tons P_2O_5 stored	Reactor, granulator, cooler, dryer, screens	0.00031 lb/hr ton			0.025[g]				88
	1,316 metric tons P_2O_5 stored	Reactor, granulator, cooler, dryer, screens	0.00035 lb/hr ton			0.027[g]				88

[a] SO_x emission factor based on the consumption and analysis of fuel oil burned in the dryer.

[b] Emissions data on file at the Florida Department of Environmental Regulation.

[c] Assuming 0.42 ton of rock is consumed in the production of 1 ton of GTSP and that GTSP product contains 46% P_2O_5 by weight.

[d] Assuming average daily production rate of 400 tons P_2O_5.

[e] Assuming that GTSP dust contains 2.5% fluoride.

[f] Assuming 24 hr/day operation.

[g] Assuming plant operates at design production capacity of 221 tons P_2O_5/day.

NOTE.—Blanks indicate emission factor not measured during test.

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(91) Granular Triple Superphosphate Storage. Contract 68-02-0232, Test Report 72-CI-30B, U.S. Environmental Protection Agency, Washington, D.C., June 1972. 32 pp.

TABLE B-8. STACK HEIGHTS FOR NSP PLANTS (72)

Plant name	Location	Main stack (mixer, den) height, m
Centrala Farmers Coop., Inc.	Forkland, AL	10.7
Gardinier, Inc.	Tampa, FL	22.3
W. R. Grace and Co.	Charleston, SC	16.8
International Minerals and Chemical Corp.	Florence, AL	24.4
	Spartanburg, SC	18.3
Kerr-McGee Corp.	Baltimore, MD	13.7
	Cottondale, FL	10.7
	Jacksonville, FL	15.5
Richmond Guano Co.	Richmond, VA	6.1
Swift and Co., Swift Chemical Co., Division	Bartow, FL	22
	Norfolk, VA	18.3
U.S. Steel Corp., USS Agri-Chemicals Division	Chicago Heights, IL	24.4
Weaver Fertilizer Co., Inc.	Norfolk, VA	15.2
The Williams Companies, Agrico Chemical Co., Inc., Subsidiary	Pensacola, FL	24.4

TABLE B-9. STACK HEIGHTS FOR GTSP PLANTS (72)

Plant name	Location	Main stack (reactor, granulator, cooler, dryer, screens) height, m
Borden Inc., Chemical Division	Piney Point, FL	61.0
CF Industries, Inc.	Plant City, FL	57.6
Gardinier, Inc.	Tampa, FL	38.4
Occidental Petroleum Corp., Occidental Chemical Co., Subsidiary	White Springs, FL	30.5
Texasgulf, Inc.	Lee Creek, NC	32.6
The Williams Companies, Agrico Chemical Co., Inc., Subsidiary	Pierce, FL	42.7

TABLE B-10. STACK HEIGHTS FOR ROP-TSP PLANTS (72)

Plant name	Location	Main stack (mixer, den, curing building) height, m
CF Industries, Inc.	Plant City, FL	30.5
Gardinier, Inc.	Tampa, FL	20.7
Royster Co.	Mulberry, FL	20.4
Texasgulf, Inc.	Lee Creek, NC	30.5

TABLE B-11. SAMPLING EMISSIONS DATA FOR AMMONIUM PHOSPHATE MANUFACTURE[a,b]

Plant	Source of emission	Controlled emission factor, g/kg P_2O_5 NH$_3$	Particulate	Total fluoride (as F)	Reference
1	Dryer		0.08		45
	Dryer		0.32		45
	Cooler		0.17		45
	Dryer		0.32		45
	Dryer		0.11		45
	Cooler		0.06		45
2	Dryer/cooler		0.32		45
3	Dryer/cooler		0.54		45
	Ammoniator		0.03		45
4	Dryer/cooler		0.16		45
	Ammoniator		<0.02		45
5	Ammoniator		<0.04		45
	Dryer/cooler		0.37		45
6	Ammoniator-granulator		1.0		45
7	Dryer/cooler		0.19		45
	Ammoniator		0.13		45
8	Dryer/cooler		0.43		45
9	Ammoniator-granulator		0.37		45
10	Ammoniator		0.40		45
11	Ammoniator		0.19		45
	Ammoniator		7.5		45
	Dryer/cooler		2.2		45
	Dryer/cooler		5.3		45
12	Ammoniator		0.48		45
13	Dryer		0.46		45
	Cooler		0.58		45
	Ammoniator		0		45
14	Ammoniator		0		45
	Dryer/cooler		0.37		45
15	Dryer/cooler		0.80		45
	Ammoniator		0		45
16	Dryer/cooler		0.36		45
	Ammoniator		<0.04		45
17	Dryer/cooler		4.1		45
	Ammoniator		0.19		45
	Ammoniator		0.13		45
16	Cooler/dryer		0.12		45
	Ammoniator		4.6		45
19	Ammoniator		0.26		45
20	Ammoniator		0.13		45
	Dryer/cooler		0.44		45
21	Ammoniator		0.89		70
	Dryer		0.12		70
22	Dryer/cooler		0.61		70
23	Dryer		0.38	0.003	^{c}
	Dryer		0.71	0.004	^{c}
	Granulator		0.05	0.003	^{c}
	Mills and screens		0.03	0.001	^{c}
24	Cooler		0.50	0.019	^{c}
	Granulator		0.13	0.019	^{c}
	Granulator		0.10	0.026	^{c}
	Cooler		0.16	0.005	^{c}
	Cooler		1.5	0.044	^{c}
	Granulator		0.47	0.028	^{c}
	Granulator		1.8	0.038	^{c}
25	Total plant	0.05			65
26	Total plant	0.14			65
27	Total plant			0.025	65
28	Total plant			0.050	65
29	Total plant			0.080	65
30	Total plant	105[d]			^{c}
31	Total plant	0.06			^{c}
32	Total plant	0.05			^{c}
33	Total plant	0.04	0.21	0.037	^{c}
	Total plant		0.15		^{c}
34	Total plant		0.09		92
35	Total plant			0.072	^{c}
36	Total plant			0.076	^{c}
37	Total plant			0.081	^{c}
38	Total plant			0.043	^{c}
39	Total plant			0.018	^{c}
40	Total plant			0.004	^{c}
41	Total plant			0.014	^{c}
42	Total plant			0.017	^{c}
43	Total plant			0.035	^{c}
44	Total plant			0.029	^{c}
45	Total plant			0.064	^{c}
46	Total plant			0.022	^{c}
47	Total plant			0.016	88
48	Total plant			0.019	88
49	Total plant			0.009	^{c}

[a] Emissions were reported in several ways, but all have been normalized to units of grams per kilogram of P_2O_5. Ammonium phosphate was assumed to be 46% P_2O_5.

[b] The number of plants identified as sampled exceeds the number of plants producing ammonium phosphates. Due to anonymity of sampling sites, multiple reportings of some plant emissions could not be eliminated.

[c] Data obtained from public files at the Florida Department of Environmental Regulation, Winter Haven, Florida, June 1976.

[d] This value was not used in determining the average emission factor since a plant with an acidic scrubber would not release this amount of ammonia under normal conditions.

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(92) Sanders, L. Monitoring and Control of Gaseous and Particulate Emissions from Fertilizer Complex. Presented at the 69th Annual Meeting of the Air Pollution Control Association (Paper No. 76-56), Portland, Oregon. July 27 to July 1, 1976. 14 pp.

APPENDIX C

MASS BALANCES

As an aid in the evaluation of emission factors, mass balances were developed for the production of NSP and TSP (ROP-TSP and GTSP). Balances were performed on the basis of phosphorus pentoxide and fluoride contents of rock, acid, and fertilizer product. Production statistics used in the equations were those reported by individual plants to the Florida Department of Environmental Regulation.

NSP

Material balances performed on the basis of phosphorus pentoxide (P_2O_5) and fluoride (F^-) involve only the rock and fertilizer product in NSP production.

Assumptions

- NSP product contains 20% P_2O_5 by weight.
- Phosphate rock contains 33% P_2O_5 and 3.8% F^-.
- Cured NSP has a fluoride content ranging from 1.41% to 2.15% (6).

The P_2O_5 balance to establish the amount of rock required, R, to produce 1 metric ton of NSP product is:

$$\left(\frac{0.33\text{ kg }P_2O_5}{\text{kg rock}}\right)(R) = \left(\frac{0.20\text{ kg }P_2O_5}{\text{kg NSP}}\right)(1{,}000\text{ kg NSP})$$

$$R = 606\text{ kg rock}$$

Result

The production of 1 metric ton of NSP requires the consumption of 0.606 metric ton of rock.

In order to estimate the amount of fluorine that is lost to the atmosphere or absorbed by the scrubbing medium, the difference between the fluoride entering with the rock and that leaving with the product is determined. Two cases will be considered in the following analysis: Case I considers cured NSP product with a fluorine concentration of 1.41%, and Case II considers a fluorine concentration of 2.15% in the product.

Case I

Fluoride entering in the rock:

$$\left(\frac{0.038\ \text{kg F}^-}{\text{kg rock}}\right)(606\ \text{kg rock}) = 23\ \text{kg F}^-$$

Fluoride in fertilizer product:

$$\left(\frac{0.0141\ \text{kg F}^-}{\text{kg NSP}}\right)(1{,}000\ \text{kg NSP}) = 14.1\ \text{kg F}^-$$

Thus 8.9 kg F^-/metric ton NSP (44.5 kg F^-/metric ton P_2O_5) is released during the production and curing operations. Therefore, a scrubber efficiency of 99% would result in an emission factor of 0.445 kg F^-/metric ton of P_2O_5 in the product.

Case II

Fluoride entering in the rock:

$$\left(\frac{0.038\ \text{kg F}^-}{\text{kg rock}}\right)(606\ \text{kg rock}) = 23\ \text{kg F}^-$$

Fluoride in fertilizer product:

$$\left(\frac{0.0215\ \text{kg F}^-}{\text{kg NSP}}\right)(1{,}000\ \text{kg NSP}) = 21.5\ \text{kg F}^-$$

Thus 1.5 kg F^-/metric ton NSP (7.5 kg F^-/metric ton P_2O_5) is released during the production and curing operations.

In this case a scrubber efficiency of 99% would result in an emission factor of 0.075 kg F^-/metric ton P_2O_5 in the product.

GTSP

Statistics for rock and acid consumption taken from those reported by Plant A:

Phosphoric acid (40% P_2O_5)	55,600 kg/hr
Phosphate rock	29,500 kg/hr

Assumptions[a]

- Phosphate rock contains 33% P_2O_5 and 3.8% F^- by weight.

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[a] Estimates based on values reported to the Florida Department of Environmental Regulation.

- Phosphoric acid contains 2.0% F^-.
- GTSP contains 46% P_2O_5 and 2.5% F^-.

The P_2O_5 balance to establish the corresponding rate of GTSP production is:

$$\left(\frac{0.33\ \text{kg}\ P_2O_5}{\text{kg rock}}\right)\left(\frac{29{,}500\ \text{kg rock}}{\text{hr}}\right) + \left(\frac{0.40\ \text{kg}\ P_2O_5}{\text{kg acid}}\right)\left(\frac{55{,}600\ \text{kg acid}}{\text{hr}}\right)$$

$$= (\text{GTSP})\left(\frac{0.46\ \text{kg}\ P_2O_5}{\text{kg GTSP}}\right)$$

$$\text{GTSP} = 69{,}500\ \text{kg/hr}$$

Results

The production of 1 metric ton of GTSP requires the consumption of 0.8 metric ton of 40% phosphoric acid and 0.42 metric ton of rock.

In order to estimate the amount of fluorine that is lost to the atmosphere or absorbed by the scrubbing medium, the difference between the fluoride entering with the rock and acid and that leaving in the production is determined.

Fluoride entering in the rock and acid:

$$\left(\frac{0.038\ \text{kg}\ F^-}{\text{kg rock}}\right)(420\ \text{kg rock}) + \left(\frac{0.02\ \text{kg}\ F^-}{\text{kg acid}}\right)(800\ \text{kg acid}) = 32\ \text{kg}\ F^-$$

Fluoride remaining in product:

$$\left(\frac{0.025\ \text{kg}\ F^-}{\text{kg GTSP}}\right)(1{,}000\ \text{kg GTSP}) = 25\ \text{kg}\ F^-$$

Thus 7 kg F^-/metric ton GTSP (15.2 kg F^-/metric ton P_2O_5) is released during the production and curing of GTSP.

A scrubber efficiency of 99% would then result in an emission factor of 0.15 kg F^-/metric ton of P_2O_5 in the product.

ROP-TSP

Statistics for rock and acid production taken from those reported by Plant A:

Phosphoric acid (56% P_2O_5)	22,000 kg/hr
Phosphate rock	12,200 kg/hr

Assumptions

- Fifty-six percent phosphoric acid contains 1.5% F^-.

- Cured ROP-TSP contains 49% P_2O_5 and 2.0% F^-.

- Phosphate rock contains 33% P_2O_5 and 3.8% F^-.

The P_2O_5 balance to establish the corresponding rate of ROP-TSP production is:

$$\left(\frac{0.33 \text{ kg } P_2O_5}{\text{kg rock}}\right)\left(\frac{12{,}200 \text{ kg rock}}{\text{hr}}\right) + \left(\frac{0.56 \text{ kg } P_2O_5}{\text{kg acid}}\right)\left(\frac{22{,}000 \text{ kg acid}}{\text{hr}}\right)$$

$$= (\text{ROP-TSP})\left(\frac{0.49 \text{ kg } P_2O_5}{\text{kg ROP-TSP}}\right)$$

$$\text{ROP-TSP} = 33{,}400 \text{ kg/hr}$$

The production of 1 metric ton of ROP-TSP requires the consumption of 0.66 metric ton of 56% phosphoric acid and 0.37 metric ton of rock.

In order to estimate the amount of fluorine that is lost to the atmosphere or absorbed by the scrubbing medium, the difference between the fluoride entering with the rock and acid and that leaving in the product is determined.

Fluoride entering in rock and acid:

$$\left(\frac{0.038 \text{ kg } F^-}{\text{kg rock}}\right)(370 \text{ kg rock}) + \left(\frac{0.015 \text{ kg } F^-}{\text{kg acid}}\right)(660 \text{ kg acid}) = 24 \text{ kg } F^-$$

Fluoride leaving in product:

$$\left(\frac{0.02 \text{ kg } F^-}{\text{kg ROP-TSP}}\right)(1{,}000 \text{ kg ROP-TSP}) = 20 \text{ Kg } F^-$$

Thus 4 kg F^-/metric ton of ROP-TSP (8.2 kg F^-/metric ton P_2O_5) is released during the production and curing of ROP-TSP.

A scrubber efficiency of 99% would then result in an emission factor of 0.082 kg F^-/metric ton of P_2O_5 in the product.

APPENDIX D

NEDS DATA BASE

Table D-1 gives the state emissions burdens for the five criteria pollutants as reported in the NEDS (72). Table D-2 is an updated version of the NEDS data as computed by MRC under EPA contract (73).

TABLE D-1. NEDS EMISSION SUMMARY BY STATE (72)

State	Mass of emissions, metric tons/yr				
	Particulates	SO_x	NO_x	Hydrocarbons	CO
Alabama	1,178,643	882,731	397,068	643,410	1,885,657
Alaska	13,913	5,874	32,757	28,389	167,357
Arizona	72,685	1,679,768	123,871	189,981	815,454
Arkansas	137,817	39,923	168,989	195,538	843,204
California	1,006,452	393,326	1,663,139	2,160,710	8,237,667
Colorado	201,166	49,188	147,496	193,456	857,781
Connecticut	40,074	168,068	155,832	219,661	897,580
Delaware	36,808	209,310	58,407	63,886	204,227
Dist. Columbia	19,451	60,630	46,824	41,789	190,834
Florida	226,460	897,381	664,794	619,872	2,695,817
Georgia	404,574	472,418	369,817	458,010	2,036,010
Hawaii	61,621	45,981	44,221	89,530	275,566
Idaho	55,499	54,387	48,552	84,230	343,720
Illinois	1,143,027	2,043,020	974,372	1,825,913	6,412,718
Indiana	748,405	2,050,541	1,371,233	600,477	2,933,780
Iowa	216,493	283,416	242,524	316,617	1,440,621
Kansas	348,351	86,974	233,987	309,633	1,002,375
Kentucky	546,214	1,202,827	419,142	326,265	1,189,932
Louisiana	380,551	166,664	442,817	1,919,662	5,633,827
Maine	49,155	144,887	76,741	122,918	376,196
Maryland	494,921	420,037	265,204	295,867	1,261,804
Massachusetts	96,160	636,466	334,379	440,481	1,682,218
Michigan	705,921	1,466,935	2,222,438	717,891	3,243,526
Minnesota	266,230	391,633	311,834	410,674	1,760,749
Mississippi	168,355	50,591	172,519	195,950	829,094
Missouri	202,435	1,152,373	448,300	413,130	1,854,901
Montana	272,688	871,235	148,405	271,824	611,061
Nebraska	95,338	58,014	101,948	127,821	569,522
Nevada	94,040	304,851	88,933	53,673	215,751
New Hampshire	14,920	86,596	67,309	88,469	256,380
New Jersey	151,768	463,736	489,216	819,482	2,877,319
New Mexico	102,785	444,310	199,181	152,057	504,249
New York	160,044	345,979	572,451	1,262,206	4,881,922
North Carolina	401,017	473,020	412,599	447,238	1,734,398
North Dakota	78,978	78,537	85,708	70,289	318,679
Ohio	1,766,056	2,980,333	1,101,470	1,153,493	5,205,719
Oklahoma	93,595	130,705	222,687	341,358	1,456,627
Oregon	169,449	36,776	135,748	234,669	929,247
Pennsylvania	1,810,598	2,929,137	3,017,345	891,763	3,729,830
Rhode Island	13,073	65,761	46,921	65,833	283,650
South Carolina	198,767	247,833	521,544	907,833	4,222,168
South Dakota	52,336	17,354	49,490	90,478	387,356
Tennessee	409,704	1,179,982	426,454	362,928	1,469,253
Texas	549,399	753,098	1,303,801	2,218,891	6,897,748
Utah	71,692	152,526	80,998	98,282	402,527
Vermont	14,587	17,751	24,286	41,980	150,510
Virginia	477,494	447,394	329,308	369,416	1,548,031
Washington	161,934	272,991	187,923	344,643	1,659,117
West Virginia	213,715	678,348	229,598	116,155	494,214
Wisconsin	411,558	712,393	408,525	523,930	1,582,869
Wyoming	75,427	69,394	72,572	55,319	303,297
U.S. totals	16,762,000	28,873,000	21,722,000	23,994,000	91,782,000

ADJUSTMENTS TO GRAND TOTAL

The U.S. summary does not include certain source categories. The following additions should be considered part of the U.S. grand total for a more accurate picture of nationwide emissions.

New York point sources	311,000	993,000	382,000	127,000	44,000
Forest wild fires	375,000	0	88,000	529,000	3,089,000
Agricultural burning	272,000	15,000	29,000	272,000	1,451,000
Structural fires	52,000	0	6,000	61,000	200,000
Coal refuse fires	100,000	128,000	31,000	62,000	308,000
Total	1,110,000	1,076,000	536,000	1,051,000	5,086,000
U.S. subtotal (above)	16,762,000	28,873,000	21,722,000	23,994,000	91,782,000
U.S. grand total	17,872,000	29,949,000	22,258,000	25,045,000	96,868,000

TABLE D-2. STATE LISTING OF EMISSIONS AS OF JULY 2, 1975 (73)

	Mass of emissions, metric tons/yr Percent of U.S. totals				
State	Particulate	SO_2	NO_x	Hydrocarbons	CO
1 ALABAMA	2002000.0	1228000.0	261600.0	342100.0	372600.0
	1.53000	1.91000	2.27000	1.29000	2.04000
2 ALASKA	16340000.0	222800.0	31990.0	140800.0	472200.0
	12.50000	0.34700	0.27700	0.53200	2.58000
3 ARIZONA	3265000.0	200200.0	75100.0	171100.0	178300.0
	2.49000	0.31100	0.65100	0.64700	0.97600
4 ARKANSAS	1619000.0	205400.0	77310.0	281700.0	225800.0
	1.24000	0.31900	0.67000	1.07000	1.24000
5 CALIFORNIA	5675000.0	2557000.0	796800.0	1914000.0	1987000.0
	4.33000	3.98000	6.91000	7.24000	10.90000
6 COLORADO	3156000.0	473300.0	116800.0	294400.0	105800.0
	2.41000	0.73600	1.01000	1.11000	0.57900
7 CONNECTICUT	365600.0	1227000.0	152200.0	259400.0	92690.0
	0.27900	1.91000	1.32000	0.98100	0.50700
8 DELAWARE	130200.0	420700.0	45720.0	77510.0	24580.0
	0.09930	0.65500	0.39600	0.29300	0.13500
9 FLORIDA	2430000.0	1755000.0	410300.0	536200.0	3502000.0
	1.86000	2.73000	3.56000	2.03000	19.20000
10 GEORGIA	2331000.0	1635000.0	294200.0	526700.0	705400.0
	1.78000	2.54000	2.55000	1.99000	3.86000
11 HAWAII	251200.0	232000.0	40790.0	62720.0	84750.0
	0.19200	0.36100	0.35400	0.23700	0.46400
12 IDAHO	2430000.0	59140.0	33220.0	163600.0	518300.0
	1.85000	0.09200	0.28800	0.61900	2.84000
13 ILLINOIS	3584000.0	3714000.0	665100.0	1343000.0	412500.0
	2.74000	5.78000	5.77000	5.08000	2.26000
14 INDIANA	2202000.0	3036000.0	414400.0	675100.0	182100.0
	1.68000	4.72000	3.59000	2.55000	0.99700
15 IOWA	2579000.0	397400.0	137700.0	400800.0	90720.0
	1.97000	0.61800	1.19000	1.52000	0.49700
16 KANSAS	3358000.0	225000.0	109900.0	742800.0	174600.0
	2.56000	0.35000	0.95300	2.81000	0.95600
17 KENTUCKY	1854000.0	1627000.0	302000.0	274600.0	219300.0
	1.42000	2.53000	2.62000	1.04000	1.20000
18 LOUISIANA	1651000.0	585800.0	219000.0	1741000.0	[illegible]39900.0
	1.26000	0.91100	1.90000	6.58000	4.60000
19 MAINE	1038000.0	770700.0	54270.0	71970.0	61430.0
	0.79200	1.20000	0.47000	0.27200	0.33600
20 MARYLAND	657300.0	1352000.0	215100.0	302300.0	163400.0
	0.50200	2.10000	1.86000	1.14000	0.89400
21 MASSACHUSETTS	802700.0	3840000.0	322300.0	463100.0	190400.0
	0.61300	5.97000	2.79000	1.75000	1.04000
22 MICHIGAN	2804000.0	3513000.0	548000.0	734000.0	299400.0
	2.14000	5.46000	4.75000	2.78000	1.64000
23 MINNESOTA	3056000.0	846800.0	185000.0	388000.0	150700.0
	2.33000	1.32000	1.60000	1.47000	0.82500
24 MISSISSIPPI	1490000.0	280300.0	87010.0	350200.0	228200.0
	1.14000	0.43600	0.75400	1.32000	1.25000
25 MISSOURI	2839000.0	1259000.0	287500.0	588400.0	268500.0
	2.17000	1.96000	2.49000	2.22000	1.47000
26 MONTANA	4975000.0	177000.0	34650.0	174200.0	230500.0
	3.80000	0.27500	0.30000	0.65800	1.26000

TABLE D-2 (continued)

		Mass of emissions, metric tons/yr Percent of U.S. totals				
	State	Partic- ulate	SO_2	NO_x	Hydro- carbons	CO
27	NEBRASKA	3049000.0 2.33000	137100.0 0.21300	50940.0 0.44200	255600.0 0.96600	59590.0 0.32600
28	NEVADA	3155000.0 2.41000	263100.0 0.40900	58500.0 0.50700	36140.0 0.13700	28700.0 0.15700
29	NEW HAMPSHIRE	326500.0 0.24900	325800.0 0.50700	36060.0 0.31300	44430.0 0.16800	30200.0 0.16500
30	NEW JERSEY	815800.0 0.62300	2922000.0 4.55000	323400.0 2.80000	786600.0 2.97000	281400.0 1.54000
31	NEW MEXICO	3548000.0 2.71000	441400.0 0.68700	109800.0 0.95200	310200.0 1.17000	49460.0 0.27100
32	NEW YORK	2704000.0 2.06000	5137000.0 7.99000	721400.0 6.25000	1353000.0 5.11000	551600.0 3.02000
33	N CAROLINA	2203000.0 1.68000	2298000.0 3.58000	338400.0 2.93000	465100.0 1.76000	371500.0 2.03000
34	N DAKOTA	2854000.0 2.18000	328700.0 0.51100	61110.0 0.53000	73930.0 0.28000	22320.0 0.12200
35	OHIO	3054000.0 2.33000	4062000.0 6.32000	785800.0 6.81000	1244000.0 4.70000	482700.0 2.64000
36	OKLAHOMA	2276000.0 1.74000	163400.0 0.25400	130000.0 1.13000	674700.0 2.55000	200800.0 1.10000
37	OREGON	2885000.0 2.20000	372500.0 0.57900	62710.0 0.54400	204800.0 0.77400	304900.0 1.67000
38	PENNSYLVANIA	3132000.0 2.39000	5603000.0 8.72000	782200.0 6.78000	1331000.0 5.03000	527000.0 2.88000
39	RHODE ISLAND	113200.0 0.08640	519900.0 0.80900	38760.0 0.33600	93730.0 0.35400	29390.0 0.16100
40	S CAROLINA	1209000.0 0.92300	1076000.0 1.67000	146300.0 1.27000	260500.0 0.98500	483900.0 2.65000
41	S DAKOTA	2861000.0 2.18000	69420.0 0.10800	18560.0 0.16100	91110.0 0.34400	23480.0 0.12900
42	TENNESSEE	1789000.0 1.37000	1307000.0 2.03000	264100.0 2.29000	340900.0 1.29000	200300.0 1.10000
43	TEXAS	9302000.0 7.10000	1817000.0 2.83000	695500.0 6.03000	4139000.0 15.60000	1501000.0 8.22000
44	UTAH	2461000.0 1.88000	285400.0 0.44400	48410.0 0.42000	112800.0 0.42600	46840.0 0.25600
45	VERMONT	292100.0 0.22300	112600.0 0.17500	13710.0 0.11900	25460.0 0.09630	14190.0 0.07770
46	VIRGINIA	1607000.0 1.23000	1388000.0 2.16000	197800.0 1.71000	415200.0 1.57000	235100.0 1.29000
47	WASHINGTON	2204000.0 1.68000	626400.0 0.97500	126300.0 1.09000	361800.0 1.37000	425500.0 2.33000
48	W VIRGINIA	1261000.0 0.96200	1455000.0 2.26000	306500.0 2.66000	172800.0 0.65300	435100.0 2.38000
49	WISCONSIN	2180000.0 1.66000	1216000.0 1.89000	231300.0 2.00000	362600.0 1.37000	161300.0 0.88300
50	WYOMING	2851000.0 2.18000	513000.0 0.79800	70570.0 0.61200	275200.0 1.04000	20870.0 0.11400
	US TOTALS	131000000.0	64300000.0	11500000.0	26400000.0	18300000.0

GLOSSARY

acidulator: Reaction vessel where wet process reaction occurs.

affected population: Number of people around a typical plant who are exposed to a source severity greater than 0.05 or 1.0.

ammoniation-granulation: Process in which a chemical reaction with ammonia is combined with the physical process of granule formation.

batch den: Enclosed compartment in which a liquid mix of acid and phosphate rock is held until solidification occurs.

becquerel: Unit of radioactivity equal to one disintegration per second, 3.7×10^{10} Bq = 1 curie.

beneficiation: Combined physical and chemical process used to concentrate the phosphate value of phosphate rock ore.

blunger (pugmill): U-shaped trough in which paddles mounted on twin contrarotating shafts agitate, shear, and knead a solid-liquid mixture to produce granules.

BPL: Bone phosphate of lime or tricalcium phosphate, $Ca_3(PO_4)_2$.

concentrated phosphoric acid (merchant-grade phosphoric acid): Product of wet process phosphoric acid manufacture, approximately 53% P_2O_5.

contact process water: Any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product.

continuous den: Slow moving conveyor belt on which the liquid mixture of acid and phosphate rock sets into a solid form.

curing: Process by which superphosphate fertilizer material is held for a period of time ranging from a few days to a number of weeks during which the acidulation reaction continues.

emission factor: Quantity of a species emitted per unit of input or product.

filtered phosphoric acid: Product of wet process phosphoric acid manufacture prior to concentration, approximately 29% P_2O_5.

fugitive emissions: Gaseous and particulate emissions that are not emitted through a primary exhaust system such as a stack.

furnace process phosphoric acid: Phosphoric acid produced by heating phosphate rock in a furnace, burning the resulting elemental phosphorus, and hydrating it to phosphoric acid.

gypsum: Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$); byproduct of the wet process reaction between phosphate rock and sulfuric acid.

gypsum pond: Liquid waste receiver with the primary purpose of separating solid gypsum ($CaSO_4$) from a liquid stream resulting from the production of phosphoric acid manufacture. Supernatant from the pond is used as a wet scrubbing liquor to remove fluorides from exhaust gases in ammonium phosphate production.

hazard factor: Value equal to the primary ambient air quality standard for criteria pollutants or to a reduced TLV; i.e., (TLV)(8/24)(1/100) for noncriteria emissions.

liming: Water treatment process using lime [$Ca(OH)_2$] to neutralize waters and precipitate impurities.

merchant-grade phosphoric acid: See concentrated phosphoric acid.

melt: Molten fertilizer.

normal superphosphate: Fertilizer which contains from 16% to 21% phosphorus pentoxide (P_2O_5) prepared by reacting ground phosphate rock with sulfuric acid.

(N-P-K): Designation of fertilizer nutrient analysis:percent total nitrogen--percent phosphorus expressed as P_2O_5--percent potassium expressed as K_2O.

run-of-pile: Solid fertilizer material of a nonuniform particle size.

representative plant: Typical plant defined to establish a base on which to evaluate the emissions of the industry. The plant has average industry parameters.

source severity: Ratio of the ground level concentration of each emission species to its corresponding ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria emission species).

superphosphoric acid: Acid produced by concentration of 54% P_2O_5 to about 70% P_2O_5.

ten-yr, 24-hr rainfall event: Maximum 24-hr precipitation event with a probable recurrence interval of once in 10 yr (as defined by the U.S. National Weather Service).

threshold limit value: Airborne concentration of substances under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect.

triple superphosphate: Fertilizer containing 45% or more phosphorus pentoxide (P_2O_5) prepared by reacting ground phosphate rock with phosphoric acid.

wet process phosphoric acid: Phosphoric acid produced by reacting sulfuric acid with phosphate rock.

CONVERSION FACTORS AND METRIC PREFIXES (93)

CONVERSION FACTORS

To convert from	to	Multiply by
Curie (Ci)	Becquerel	3.700×10^{10}
Degree Celsius (°C)	Degree Fahrenheit	$t^\circ_F = 1.8\ t^\circ_C + 32$
Joule (J)	British thermal unit	9.479×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilogram (kg)	Ton (short, 2,000 lb mass)	1.102×10^{-3}
Kilometer^2 (km^2)	Acre	2.471×10^{-4}
Kilometer^2 (km^2)	Mile^2	3.861×10^{-1}
Meter (m)	Foot	3.281
Meter^2 (m^2)	Acre	2.471×10^{-4}
Meter^2 (m^2)	Foot^2	1.076×10^{1}
Meter^3 (m^3)	Liter	1.000×10^{1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Metric ton	Ton (short, 2,000 lb mass)	1.102
Pascal (Pa)	Atmosphere	9.869×10^{-6}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Pascal-second (Pa-s)	Poise	1.000×10^{1}
Second (s)	Minute	1.667×10^{-2}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	5 km = 5×10^3 meters
Centi	c	10^{-2}	5 cP = 5×10^{-2} poise
Milli	m	10^{-3}	5 mg = 5×10^{-3} gram
Micro	µ	10^{-6}	5 µg = 5×10^{-6} gram
Pico	p	10^{-12}	5 pCi = 5×10^{-12} curie

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(93) Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^\varepsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

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